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PROCEEDINGS OF THE SECOND STATIONARY SOURCE COMBUSTION SYMPOSIUM

Volume III. Stationary Engine, Industrial Process Combustion Systems, and Advanced Processes

Interagency
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16. ABSTRACT

The proceedings document the 50 presentations made during the Second Stationary Source Combustion Symposium held in New Orleans, LA, August 29-September 1, 1977. Sponsored by the Combustion Research Branch of EPA's Industrial Environmental Research Laboratory--RTP, the symposium dealt with subjects relating both to developing improved combustion technology for the reduction of air pollutant emissions from stationary sources, and to improving equipment efficiency. The symposium was divided into six parts, and the proceedings were issued in five volumes: Volume I--Small Industrial, Commercial, and Residential Systems; Volume II--Utility and Large Industrial Boilers; Volume III--Stationary Engine, Industrial Process Combustion Systems, and Advanced Processes; Volume IV--Fundamental Combustion Research; and Volume V--Addendum. The symposium was intended to provide contractor, industrial, and Government representatives with the latest information on EPA inhouse and contract combustion research projects related to pollution control, with emphasis on reducing nitrogen oxides while controlling other emissions and improving efficiency.

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PROCEEDINGS OF THE SECOND STATIONARY SOURCE COMBUSTION SYMPOSIUM

Volume III. Stationary Engine, Industrial Process Combustion Systems, and Advanced Processes

Symposium Chairman Joshua S. Bowen
Vice-Chairman Robert E. Hall

Environmental Protection Agency
Office of Research and Development
Industrial Environmental Research Laboratory
Research Triangle Park, North Carolina 27711

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PREFACE

These proceedings document the more than 60 presentations and discussions of the Second Symposium on Stationary Source Combustion held August 29 - September 1, 1977, at the Marriott Hotel in New Orleans, Louisiana. Sponsored by the Combustion Research Branch of the EPA's Industrial Environmental Research Laboratory-Research Triangle Park, the symposium presented the results of recent research in the areas of combustion processes, fuel properties, burner and furnace design, combustion modification, and emission control technology.

Dr. Joshua S. Bowen, Chief, Combustion Research Branch, was Symposium Chairman; Robert E. Hall, Combustion Research Branch, was Symposium Vice-Chairman and Project Officer. The Welcoming Address was delivered by Dr. John K. Burchard, Director of IERL-RTP; the Opening Address was delivered by Robert P. Hangebrauck, Director, Energy Assessment and Control Division, IERL-RTP; and Dr. Howard B. Mason, Program Manager NO_x Environmental Assessment Program, Acurex Corporation, delivered the Keynote Paper.

The symposium consisted of six sessions:

Session I: **Small Industrial, Commercial and Residential Systems**
Robert E. Hall, Session Chairman

Session II: **Utility and Large Industrial Boilers**
David G. Lachapelle, Session Chairman

Session III: **Special Topics**
David G. Lachapelle, Session Chairman

Session IV: **Stationary Engine and Industrial Process Combustion Systems**
John H. Wasser, Session Chairman

Session V: **Advanced Processes**
G. Blair Martin, Session Chairman

Session VI: **Fundamental Combustion Research**
W. Steven Lanier, Session Chairman

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SESSION IV:

STATIONARY ENGINE AND INDUSTRIAL PROCESS COMBUSTION SYSTEMS

JOHN H. WASSER
CHAIRMAN

APPLICATION OF COMBUSTION MODIFICATIONS TO INDUSTRIAL COMBUSTION EQUIPMENT

By:

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ABSTRACT

This is a report of a research program to evaluate the effectiveness of combustion modifications as means of emissions reduction and thermal efficiency improvement on industrial combustion equipment. A survey conducted to determine important and representative industrial equipment resulted in selection of combustion devices for test in the petroleum refining, minerals, paper, and metals industries. This report presents results of tests on petroleum refinery heaters, mineral kilns, metal furnaces, boilers burning unconventional fuels, internal combustion engines, and gas turbine combined cycles. Test results from two modified industrial boilers are also included.

The effects of process variables, excess air reduction, burner adjustments, staged combustion and fuel type were the main techniques evaluated. The results indicated that these techniques, developed primarily on conventional steam boilers, are also effective in emissions control on certain devices but some devices were completely unresponsive. Critical process temperatures, chemistry and fluctuations represent the main constraints and the effectiveness of combustion modifications is primarily dependent on process flexibility.

This report was submitted in fulfillment on Contract 68-02-2144 by KVB, Inc. under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period January 23, 1976 to May 23, 1977.

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SECTION 1

INTRODUCTION

Combustion modifications have been applied for many years to control emissions, primarily of NO_x, from large utility boilers. This paper presents results of an investigation of the applicability of combustion modifications to industrial combustion equipment other than boilers burning conventional fuels. Twenty-two devices were tested in sixteen facilities under conditions of practical production constraints.

The need to control nitrogen oxides (NO_x) from large fossil-fuel steam generators has resulted in the development of techniques for combustion modification to reduce gas temperatures and alter mixing rates in a manner which reduces NO_x without operational disruption. These techniques are well documented and recently reviewed (Refs. 1, 2, 3). There is also a developing technology in the use of flue gas treatment to remove NO_x (Refs. 4, 5).

The estimates of NO_x emissions for the major stationary sources, as shown in Table 1, clearly show that steam boilers burning conventional coal, oil and gas fuels are the predominant stationary sources of NO_x emissions. It is therefore clear why the main thrust of efforts to control NO_x emissions has been concentrated on these sources, primarily the larger size units. Further efforts to extend controls on steam boilers to lower levels of emissions or to smaller size units can be expected to incur greater costs per unit of NO_x emissions reduced.

As indicated in Table 1, there are a variety of sources other than steam boilers that contribute significantly to national NO_x emissions. As controls become more costly for steam boilers, it is important to examine the potential for control on these other sources to determine whether more cost-effective options for NO_x control can be identified. Before the cost effectiveness of various control options can be firmly established, it is necessary

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to quantify the emissions at normal operating conditions and to demonstrate the applicability and emissions reduction potential of the various control techniques.

As indicated in Table 1, comparison of the three sets of estimates for NO_x emissions show fairly good agreement for the steam boiler categories. For other categories, there are much greater differences, with some categories completely missing. Some of the discrepancies are believed to be the result of difference in the approach to classifying sources. Other discrepancies are due to inadequate information on inventories, consumption rates and emission factors. It was not the purpose of this study to resolve these discrepancies, but it may provide some information that may assist in that resolution. The basic purpose of this study was to begin the task of investigating the applicability of combustion modifications for control of emissions on industrial combustion devices.

OBJECTIVE AND SCOPE

The objective of the program was to investigate the effectiveness of combustion modifications and operating variable changes as means for emissions control and improvement in thermal efficiency on a variety of industrial combustion devices. These techniques have previously been shown to be effective on industrial boilers and the purpose of this program was to investigate the basic feasibility and/or limitations for application of this technology to other industrial combustion devices.

The program scope provided for tests on about 25 industrial combustion devices representative of kilns, ovens, dryers, process furnaces, boilers, stationary engines and gas turbines in use. Emissions measured included NO, NO_2, SO_2, SO_3, CO, CO_2, gaseous hydrocarbons, particulates, particle size distribution, smoke number, and opacity. On selected devices, samples were collected for analysis of trace species and organics emissions. Combustion modifications to be evaluated where possible included lowered excess air, staged combustion, reduced air preheat, water injection, and flue gas recirculation.

In addition to tests on the selected industrial combustion devices, two modified industrial boilers that had previously been tested for EPA (Ref. 3) were retested to develop new data on the combined effects of several combustion modifications.

SECTION 2

TEST UNIT SELECTION AND DATA SUMMARY

A survey was conducted to establish representative units in a number of industrial activities and to prioritize the devices so that test results would have the widest applicability and be of most significance in regard to national emissions from stationary sources.

A prior study for EPA formed the basis for initial selection of the industries for evaluation (Ref. 5). This was augmented with emissions data from the NEDS system, industry energy consumption data and contact with industry associations, manufacturers, and equipment users. Further information was developed on specific designs as a basis for selection of the specific test units. From an initial list of 35 units desired for test, all types were tested with the exception of a glass furnace, a blast furnace gas boiler and a simple cycle gas turbine.

The device types that were tested and a brief summary of NO_x emissions, reductions and control methods are shown in Table II. In general the results indicate that combustion modifications can be applied to industrial combustion equipment but reductions achievable vary significantly for different types of devices. Reductions in NO_x of up to 79% were observed but on many devices reductions were less than 10%.

As a group, the devices considered number in the several thousands. Because of the wide diversity in design approach, it was not possible to define completely representative or typical devices. The test results cannot, therefore, be interpreted as representative in a firm statistical sense, of emission levels or efficiency of specific device groups as a whole. Rather, the results are intended to serve the primary program objective: investigation of the feasibility and effectiveness of combustion modifications by definition of those modifications that offer the most promise for further investigation and application.

SECTION 3

INSTRUMENTATION

The emission measurements were made using analytical instruments and equipment contained in a government-furnished mobile instrumentation laboratory. Gaseous samples were extracted from exhaust stacks through two lines. One was heat-traced and maintained at 350 °F to prevent loss of NO_2, SO_2, and hydrocarbons that are soluble in water. A second unheated line supplied sample gas to the remaining instruments. Gaseous emission measurements were made with instruments listed in Table III. All instruments were calibrated at regular intervals with calibration gases carried in the mobile laboratory.

On devices that had adequate stack sampling ports (3 to 4 inches I.D.), measurements were made of particulate by EPA Method 5, and particulate size distribution with cascade impactors (Brinks Model B for high particulate loading or an Anderson 2000 Mark III for low loadings). Samples were taken by the Shell-Emeryville method and titrated for SO_2 and SO_3. Smoke numbers were recorded with the Bacharach Smoke Spot Sampler, and stack opacity was measured by EPA Method 9.

All pertinent process data was recorded including data necessary to determine thermal efficiency.

Samples were collected for analysis of trace species and organics by the use of the EPA Source Assessment Sampling System (SASS) and procedures defined by EPA for environmental assessment (Ref. 10). However, the current program requirements were not specifically formulated in terms of the complete environmental assessment objectives.

SECTION 4

COMBUSTION MODIFICATIONS ON INDUSTRIAL COMBUSTION EQUIPMENT

This section summarizes the design capacities, fuels, used baseline emissions, combustion modifications that were applied and reductions obtained for tests on 22 industrial combustion devices. Results for common types of devices are grouped together in the section in the following order:

Petroleum Process Heaters
Mineral Kilns (Clay and Cement)
Metal Furnaces (Steel and Aluminum)
Boilers Burning Unconventional Fuels
Internal Combustion Engines
Gas Turbine Combined Cycle Systems

Complete presentation of all emissions and efficiency data was not possible in this paper because of the large amount of data obtained and the wide diversity of equipment types represented. The results are presented primarily in terms of the effect on NO_x emissions as this emissions is the one that is most affected by combustion modifications. The test program was completed in May 1977 and a final report for the program will be issued shortly.

COMBUSTION MODIFICATIONS ON PETROLEUM PROCESS HEATERS

Natural Draft Heaters

Five of the seven heaters tested in this program were vertically fired natural draft types of box construction. The number of burners ranged from 10 to 32 and heat input rates varied from 11 to 26 MW (36 to 87 MMBtu/hr). All the units had burners sized at about 0.94 ± 0.14 MW (3.2 ± 0.5 MMBtu/hr) per burner. Process types included flasher heating, reforming, and recycle gas heating.

The baseline (unmodified) NO_x emissions expressed as NO_2, for the five natural draft heaters firing refinery gas were 47 ± 9 ng/J (0.11 ± 0.02 lb/MMBtu or 92 ± 17 ppm)[1]. These emission levels are consistent with other data from a recent program in which baseline emissions on 26 heaters were measured (Ref. 11). However, these levels are significantly lower than the standard EPA emission factor (Ref. 12) of 0.23 lb of NO_x/MCF (0.22 lb/MMBtu or 95 ng/J) for refinery boilers and heaters firing gaseous fuel. This factor was based on data taken in 1958 (Ref. 13).

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[1] 1 lb/MMBtu = 430 ng/J = about 840 ppm with gas fuel or 750 ppm with oil fuel, dry volume corrected to 3% O_2. All ppm values are corrected to 3% O_2, dry.

Modifications made to the natural draft heaters included:

1. Fuel heat content variation
2. Load variation
3. Burner air register adjustments
4. Staged combustion by removal of burners from service

Fuel Heat Content Variation--

The first heater tested (Site 4) was a flasher heater of double box construction. Following baseline tests the refinery fuel gas system was adjusted to eliminate natural gas. Propane was injected to increase the heating value. NO_x emissions increased about 7% to 48 ng/J (94 ppm, 3% O_2, dry) from a baseline level of 45 ng/J (88 ppm). Fuel gas analysis indicated the propane content was increased from about 7% to 16% resulting in a 17% increase in heating value. Prior work had attributed large changes in NO_x to changes in fuel gas composition (Ref. 11), however not every unit tested exhibited that sensitivity. The test for the current program indicates that NO_x increases with increase fuel heating value but not to a significant degree. However, more study is needed on different heaters over a wider range of heating value.

Load Variation--

Two heaters that were part of a catalytic reformer process were tested (site 5) during process rate changes of ± 20%. NO_x emissions were observed to decrease as load increased (Fig. 1). At the lowest load, NO_x emissions were about 51 ng/J (100 ppm) for both heaters. At the highest load one heater emitted 41 ng/J (80 ppm) and the second about 31 ng/J (60 ppm). Excess air was reduced as load increased and that was the most probable reason for the NO_x reduction.

Burner Adjustments--

Air register adjustments and removal of burners from service were done to attempt to achieve staged combustion by creating fuel-rich and fuel-lean regions in the flames. This can reduce flame temperatures and lower the NO_x formation rates. The procedure involves removing about 25% of the burners from service and then optimizing air registers for lowest NO_x. Various combinations of burners out of service are tested to find an optimum pattern.

Five different burner patterns were implemented on a double furnace heater (site 4). One pattern was found that reduced NO_x from about 59 ng/J (116 ppm) to 49 ng/J (95 ppm), an 18% reduction. The other patterns produced only about a 10% reduction (Fig. 3). These reductions are not considered particularly significant because of fluctuations in baseline levels that were about the same magnitude as the reductions. The fluctuations were probably due to fuel gas property changes.

The second heater tested (site 5/1) was operating at 50% load and had only six burners, of sixteen total, in service. Adjustment of the air registers reduced NO_x by 20%. Placing two more burners in service (8 total) increased NO_x emissions by 14% from the baseline level. The third heater tested (site 5/2) had only four burners (of ten total) in service. No pattern tests were attempted but air register adjustment did not produce any change in NO_x.

On the fourth heater (site 7/1), adjustment of the air registers reduced NO_x about 20% but removing two burners from service had no effect. The fifth heater (site 7/2) had badly corroded air registers so that no register adjustments could be made.

The response of natural draft process heater NO_x emissions to burner adjustments was found to be poor compared to previous results on boilers. One reason is that in most cases the burner removal patterns resulted in increased excess air which could not be lowered to baseline levels because of furnace pressure limits. Also the design of natural draft burners utilizes the fuel flow as an aid to induce combustion air and this acts to defeat the attempt to achieve staged combustion. Furthermore, the in-line vertically-fired burner arrangement used for most heaters does not provide much inter-burner mixing, a necessary feature of staged combustion. Further work on burner hardware modifications will be necessary to determine whether these limitations can be ov

Mechanical Draft Heaters

Of the two mechanical draft heaters tested, one had combustion air preheat. Both were vertical cylindrical types and were tested while firing refinery gas or Number 6 fuel oil through a single combination gas and oil burner in each heater. The only adjustment that could be made was variation of excess air. Staged combustion could not be done because of the single burner.

Operation of the heater that had air preheat (site 12/1), while firing refinery gas, produced NO_x emissions of about 163 ng/J (320 ppm) or about three times that of natural draft heaters. Variation of excess air showed a tendency for reduced emissions as excess air was reduced. When firing Number 6 oil, NO_x emissions were 30% lower than for gas fuel. Variation of excess air, firing oil, did not result in any significant change in NO_x, as shown in Figure 3.

The mechanical draft heater without air preheat (site 12/2), operating on refinery gas, experienced large fluctuations in NO_x from about 43 to 109 ng/J during initial testing. This was probably due to fuel gas property changes. During later tests NO_x stabilized at about 64 ng/J (126 ppm) with 5% excess oxygen. Reduction of excess oxygen to 2% reduced NO_x to 36 ng/J, a 44% reduction. Operation of this heater with Number 6 oil resulted in NO_x emissions of about 92 ng/J (164 ppm) and, as with the preheated unit, variation of excess air did not result in any significant change in NO_x.

COMBUSTION MODIFICATION ON MINERAL KILNS

One tunnel kiln for manufacture of clay tile pipe and two rotary kilns for making Portland cement clinker were tested.

Clay Tile Pipe Tunnel Kiln

A tunnel kiln is a long insulated tunnel through which clay pipe is moved on cars. Burners along the tunnel walls provide a programmed temperature firing cycle of heating, soaking, and cooling. The kiln tested (site 1) had 14 combination gas and oil burners per side with a total rated heat input of 9.4 MW (32 MMB/h). Tests were conducted at about 80% of rated capacity.

The baseline NO_x emission firing natural gas was 46.2 ng/J (90 ppm) and particulate was 12.5 ng/J (0.029 lb/MMBtu). Oxygen levels were measured at various points within the kiln and varied from about 0.2 to 11% in the main heating zone.

Adjustment of burner excess air was planned. However even slight changes in burner fuel to air ratio cause significant changes in kiln temperature that adversely affect product quality. This type of kiln therefore appears to have very little flexibility for combustion modification.

Dry Process Rotary Cement Kiln

Cement kiln processes in the U.S. are about equally divided between dry and wet processes. In the dry process, feed materials are fed to the kiln as a dry finely-divided powder while in the wet process the feed is mixed with water to form a slurry. One of each process type was tested.

The dry process kiln tested (site 3) was rated at a heat input of 77.8 MW (265 MMB/hr) and was tested at full capacity while firing a mixture of coke (68%) and natural gas (32%). Previous data (Ref. 6) were available for this kiln firing natural gas and oil separately. The purpose of the test was to evaluate fuel switching as an NO_x emission control method. Emissions of NO_x while firing natural gas were 1050 to 1800 ng/J (1680 to 2900 ppm). Operation on oil reduced NO_x to 400-710 ng/J (600-1085 ppm), a reduction of 60%. Operation on combined coke (68%) and gas (32%) produced NO_x emissions of 655-710 ng/J (950-1014 ppm), a 50% reduction. The coke fuel burned in these tests contained 2.4% fuel nitrogen (equivalent to 1635 ng/J for 100% conversion) at the tested 68% of total heat input. Therefore the measured emissions are from 24 to 43% of the theoretical fuel nitrogen emission rate. Actual fuel nitrogen conversion is probably much lower because some of the measured NO_x was undoubtedly due to thermal formation.

Lower NO_x emissions on solid and liquid fuels compared to gas are attributed to the highly adiabatic nature of the process. Many cement kilns are currently being converted from gas to solid fuels. This conversion will be beneficial in reducing NO_x and could be pursued as an NO_x control method that is consistent with the reduction of industrial gas consumption.

Wet Process Cement Kiln

The wet process cement kiln tested (site 9) was rated at 9.44 kg/s (185 tons/d) of cement clinker with a heat input rate of 61 MW (210 MMBtu/hr) and only operated on natural gas. Baseline NO emissions were 1319 ng/J (2250 ppm) and particulate emissions upstream of an electrostatic precipitator were 11000 ng/J (26 lb/MMBtu). Particulate sizing indicated that 17 percent was less than 1 μm.

Combustion modifications investigated included variation of combustion air inlet temperature and excess oxygen. Increase of combustion air temperature from 644 K (750 °F) to 767 K (920 °F) increased NO emissions to 1510 ng/J, a 15% increase. Reduction of excess oxygen at baseline air temperature reduced NO to 846 ng/J, a 36% reduction. The independent reductions of either excess air or air temperature caused unacceptable reduction of kiln temperature that can result in a process upset. The NO emission was found to be a strong function of kiln temperature, shown in Figure 4. It was found that simultaneous reduction of excess air and increase in air temperature could produce a reduction in NO of about 14% while maintaining kiln temperature.

COMBUSTION MODIFICATIONS ON METAL FURNACES

Metal furnaces tested included a steel open hearth furnace, a steel billet reheat furnace, a steel ingot soaking pit and a scrap aluminum melting furnace.

Steel Mill Open Hearth Furnace

Steel mill open hearth furnaces are being gradually phased out in favor of the basic oxygen process. However, the open hearths have more flexibility in charge composition and may remain a significant source of NO_x in areas where their use is continued (Ref. 9).

One open hearth unit was tested (site 14) while operating on combined natural gas (60%) and Number 6 oil (40%). The rated heat input is 57.2 MW (195 MMBtu/hr) and steel batch production is 3×10^5 kg (335 tons) per heat cycle of 7 hours.

Gaseous emissions were measured between a waste heat boiler and an electrostatic precipitator over a full heating cycle without modification. Wide fluctuations in NO_x and CO were observed as various operations were performed as shown in Figure 5. Large changes in excess air occurred as the operators opened doors to look at the steel and to add material or adjust fuel flow to change heating rate. NO_x emissions varied from 100 to 3500 ppm and averaged about 1800 ppm or about 950 ng/J (2.2 lb/10^6 Btu). NO_x increased somewhat linearly with excess O_2. Particulates emissions were 2200 ng/J (5.02 lb/MMBtu), measured upstream of the precipitator. Following baseline tests the furnace was overhauled to repair refractory, fix leaks, etc. A second test cycle was observed on the repaired furnace and the average NO_x was 1094 ng/J (2070 ppm), very close to the first cycle measured. A third cycle was observed during which the excess air was controlled to minimize large increases. The average NO_x emission was reduced to 660 ng/J (1250 ppm), a reduction of about 40%. During baseline tests NO_x frequently exceeded 2000 ppm but with the excess air controlled, excursions over 2000 ppm occurred only twice.

Steel Billet Reheat Furnace

One steel billet reheat furnace was tested (site 16/1) while firing natural gas. The rated heat input is 35 MW (117 MMBtu/hr) and tests were conducted at from 13 to 30 MW. Baseline NO_x emission at 24 MW was 56 ng/J (110 ppm) and particulates were 17 ng/J (0.04 lb/MMBtu). This furnace had two heating zones with 13 and 14 burners, respectively. The row with 13 burners released about 80% of the heat input. Combustion modifications included reduced excess air, resulting in a 24% NO_x reduction, and burners out of service which produced a 43% NO_x reduction with 3 burners out of service in the row of 13 burners.

Steel Ingot Soaking Pit

One steel ingot soaking pit was tested (site 16/2) while firing natural gas. The rated heat input is about 2.9 MW (10 MMBtu/hr) fired through a single burner. Baseline NO_x emissions at 2 MW was 52 ng/J (101 ppm) and reduction of excess air reduced NO_x by 69% with no adverse effect on the steel.

Scrap Aluminum Melting Furnace

The furnace tested (site 6) is a 39 Mg (43 ton) batch charged unit used to melt scrap aluminum during a four to six hour cycle. Two package burners fire natural gas or Number 2 oil at a rated heat input of 9.8 MW (33.6 MMBtu/hr). Baseline NO_x emissions were 49 ng/J (96 ppm) on natural gas and 104 ng/J (185 ppm) on Number 2 oil. Adjustment of excess air was the only modification possible and reduction of excess air produced a slight increase of 4 to 15% in NO_x on both gas and Number 2 oil.

COMBUSTION MODIFICATIONS ON BOILERS FIRED WITH UNCONVENTIONAL FUELS

Four boilers were tested that fire fuels other than natural gas, oil, or coal. These included one paper mill boiler fired on black liquor, two paper mill wood bark waste boilers, and one petroleum refinery boiler fired with carbon monoxide gas.

Paper Mill Black Liquor Recovery Boiler

Black liquor is the waste liquid from the wood digestion process. It contains sodium inorganics, water and lignin organics dissolved from the wood. The sodium is recovered for reuse by spraying the liquor into a boiler. The organics are burned and the sodium sulfate is reduced to sodium sulfide ash which is removed from the boiler floor. Black liquor recovery boilers differ significantly in design from conventional boilers in requiring a reducing atmosphere near the bottom and an oxidizing atmosphere in the upper part of the furnace. Natural gas (or oil) is frequently used for ignition and load stabilization.

The boiler tested (site 10/2) is rated at 97522 kg (215,000 lb) per hour of steam flow. The combustion analysis for black liquor is a complex chemical balance. Data were obtained but analysis has not been completed at the time of this paper. It is therefore possible to provide emissions only in terms of concentrations. Baseline NO_x emissions were relatively low, 52 ppm, but hydrocarbons were high, 900 to 2700 ppm and CO was up to 30,000 ppm.

Combustion modification was limited to adjustment of secondary (upper stage) air adjustment and reduction of black liquor solids content. Secondary air adjustment reduced NO_x by 33% but increase hydrocarbons by 200%. Adjustment of liquor solids content had little effect on emissions.

The intimate connection of this type of boiler to the chemical processes in the paper mill, and the complexity of the chemical process indicate that achievement of emissions reduction by combustion modification will be considerably more difficult than for conventional boilers.

Wood Bark Boilers

Of two wood bark boilers tested, the first (site 10/1) was rated at 91000 kg (200,000 lb) per hour steam flow with a traveling grate stoker firing wood and natural gas. Difficulties were experienced with fluctuating wood feed rates. Baseline NO_x was 124 ng/J (229 ppm) corrected to 3% O_2. Particulate emissions upstream of the precipitator were 1334 ng/J (3.0 lb/MMBtu). Only 5% of the particulate is less than 3 µm. Combustion modifications included air preheater bypass, burner adjustments, and staged combustion by burner shut-off. Lower excess air reduced NO_x to 75 ng/J (138 ppm). Air preheater bypass did not significantly lower emissions since O_2 content was increased. Shut-off of one of the four burners reduced NO_x about 20%.

The second wood bark boiler (site 13) was rated at 45400 kg (100,000 lb) per hour steam flow and fired wood and coal with an overfeed traveling grate stoker. During the test the boiler was firing about 25% bark and 75% Kentucky coal. At peak bark flow, baseline NO_x emissions were 169 ng/J (226 ppm). Termination of bark flow increased NO_x to 232 ng/J (367 ppm). Baseline total particulate emissions were 166 ng/J (0.38 lb/10^6 Btu) and 40% of the particulate was less than 3 µm aerodynamic diameter. Variation of excess air resulted in a reduction in NO_x of 15% with an NO_x range of 160 to 250 ng/J. The unit normally operates with overfire air ports 100% open. Closing these ports to 30% open reduced NO_x by 18%. This behavior is contrary to most other boilers and was attributed to observed changes in the point in the furnace where the bark combustion took place.

It was concluded that wood bark boilers are similar to coal fired boilers in response to combustion modification with the exception that wide fluctuations in bark flow make it difficult to attain steady conditions.

Carbon Monoxide Boiler

The catalytic cracking process in manufacture of gasoline generates an off gas that contains about 10% carbon monoxide. This gas is used as a fuel to fire boilers both to control emissions of CO and to provide steam.

The one CO gas boiler tested (site 11) was rated at 136000 kg (300,000 lb) per hour of steam flow and had four spud type gas burner. It was also equipped with staged air ports. Baseline NO_x emissions were 61 ng/J (126 ppm). Baseline particulate emissions were 129.3 ng/J (0.301 lb/MMBtu). Lowering excess air reduced NO_x by 8% for a decrease in O_2 from 3.1 to 1.8%. Adjustments in NO_x ports changed NO_x less than 2%. Burners out of service did not result in any decrease in NO_x. CO emissions were much more sensitive to excess oxygen with large increases in CO level being measured below about 2.0% O_2.

The lack of response of NO_x to combustion modifications is attributed to NO_x that is formed from ammonia in the CO gas feed acting similarly to fuel nitrogen in oil or coal.

COMBUSTION MODIFICATIONS ON INTERNAL COMBUSTION ENGINES

Two reciprocating internal combustion engines were tested. One drove a natural gas compressor in a gas processing plant and the second was a diesel engine driving an electric generator.

Natural Gas Compressor Engine

This engine (site 2) was an eight cylinder, 2 cycle, naturally aspirated engine rated at a shaft power of 660 kW (880 hp) at 260 RPM and fired with natural gas. Baseline NO_x emissions were 1020 ng/J (1990 ppm), CO was 1150 ppm and hydrocarbons were about 14000 ppm (mostly unburned fuel or methane).

Combustion modifications included load and speed variation and adjustment of fuel and air. Load could only be adjusted about ± 6% and this produced a decrease in NO_x of about 5% for both the increase or decrease in load away from baseline. Increasing speed from 260 RPM to 300 RPM reduced NO_x by 10%. Fuel to air ratio adjustment war difficult because each cylinder had separate adjustments and when these adjustments were changed there was no apparent change in excess O_2. However NO_x was decreased by 20% and hydrocarbons were reduced by about 50% by the adjustments made.

Diesel Electric Generator

The diesel generator engine (site 15) was a 4-stroke cycle, turbocharged, aftercooled, engine with twelve cylinders and rated at 600 kW at 1200 RPM. Baseline load was 400 kW operating with No. 2 diesel fuel. NO_x emissions were 830 ng/J (1476 ppm) and total particulates were 49 ng/J (0.114 lb/MMBtu). Combustion modifications included variation of engine load and inlet air temperature. Reduction of load to 200 kW did not produce any change in NO_x but, at 100 kW, NO_x was reduced by 14%. Reduction of the inlet air temperature, by increased turbocharger aftercooling, from the baseline of 356 K (180 °F) to 344 K (160 °F) only reduced NO_x by 7%.

Conclusions

It was concluded that in-field modifications on internal combustion produce only small changes in emissions, at least for engines tested.

COMBUSTION MODIFICATIONS ON GAS TURBINE COMBINED CYCLE UNITS

No gas turbines operating in industrial plants were located on which combustion modifications could be made directly to the gas turbine. Engines with water injection are located primarily in electric utilities and have been extensively tested in other programs. Some industrial gas turbines are equipped with fired waste heat boilers and two of these were tested to evaluate the potential the use of staged combustion as a means of reducing total NO_x. A previous laboratory scale study had indicated the potential for destruction of NO_x from the gas turbine by staged combustion in the boiler (Ref. 14).

Petroleum Refinery Combined Cycle

The first combined cycle system tested (site 7/3) consisted of a 12.5 MW gas turbine with a boiler rated at 23660 kg (515,000 lb) per hour steam flow. Both units used refinery gas fuel. Baseline NO_x emissions from the gas turbine at 10 MW were 96.9 ng/J (190 ppm, 3% O_2) and from the boiler at 91% steam flow were 59.2 ng/J (118 ppm, 3% O_2). The heat input for "Joules" in ng/J is based only on the gas turbine fuel for gas turbine emissions but is based on the total fuel to both gas turbine and boiler for the boiler exit emissions. The gas turbine fuel heat release was 20.7% of the total fuel heat input. Therefore, the NO_x mass flow from the gas turbine was increased by 200% in the boiler.

Combustion modifications performed on the boiler consisted of air register adjustments and removal of one of the eight burners from service. Air register adjustment reduced boiler stack CO from 401 ppm, 3% O_2 at base- line to 12 ppm but increased NO_x by 8%. Removal of the burner from service decreased boiler stack NO_x by 14%. This translates to a 156% increase in NO_x mass flow by the boiler, a 22% reduction in added NO_x formed in the boiler.

Chemical Plant Combined Cycle

The second combined cycle system tested (site B) consisted of a 15 MW gas turbine with a boiler rated at 697500 kg (1.538 x 10^6 lb) per hour steam flow. Both units fired refinery gas and the boiler could fire oil. Baseline NO_x emissions firing gas in both units from the gas turbine at 76% load were 83.8 ng/J (166 ppm, 3% O_2) and, from the boiler at 70% load, were 52 ng/J (103 ppm, 3% O_2). On a mass flow basis the NO_x mass flow increased by 195% in the boiler. These levels are nearly identical to the petroleum refinery com- bined cycle system discussed above. When the boiler was switched to No. 2 oil the total NO_x emissions increased to 64 ng/J (114 ppm, 3% O_2) or a 213% addition to NO_x mass flow over the gas turbine emission rate.

Modifications (on gas only) consisted of air register adjustments and removal from service of 2 and 4 of the 16 boiler burners. Air register adjust- ment had no influence. Removal of 2 burners reduced total NO_x by 12% and removal of 4 burners reduced total NO_x by 38%. The latter represents a 91% addition to total NO_x mass flow over the gas turbine NO_x mass flow. Relative to the 213% addition to NO_x measured at baseline, a 55% reduction was obtained in NO_x created by the boiler.

Conclusions

It was not possible to determine whether any gas turbine NO_x was being destroyed in the boiler fuel-rich regions, indicated as possible in a prior study (Ref. 14). That study suggested the possibility that total NO_x mass flow from the boiler stack could be reduced below the mass flow level of the gas turbine. The present data do not support that conclusion. However the large (55%) reduction in the NO_x added by the boiler when only 4 of 16 burners were removed from service strongly indicate that some gas turbine NO_x destruction may have occurred.

SECTION 5

COMBUSTION MODIFICATIONS OF MODIFIED INDUSTRIAL BOILERS

During a previous program with EPA, KVB tested two industrial boilers that had been modified to provide staged air (in both boilers) and flue gas recirculation (in one boiler). Results of those tests were presented in the report of that work in which the boilers are identified by test location numbers 19 and 38 (Ref. 3). Additional tests have been conducted on these boilers as part of the current program to attempt to extend the reductions previously achieved, evaluate modifications in combination and resolve some limitations that were found.

COMBINED COMBUSTION MODIFICATIONS AT LOCATION 19

The boiler at location 19 was a single-burner oil- and gas-fired watertube unit rated at 7700 kg (17000 lb) per hour steam flow with no economizer or air preheater. The tests were run at 83% of full load. Second-stage combustion air was injected through four steel lances which were inserted through the windbox and the refractory firing face. Flue gas was withdrawn from the base of the stack and was added to the burner air through wide slots just upstream of the burner throat.

Baseline emissions of NO_x were as follows:

Fuel	NO_x, ppm, 3% O_2 dry
Natural gas (Ring burner)	96
(Gun burner)	92
No. 2 oil (less than 0.01% N)	110
No. 6 oil (0.30% N)	221

Oil atomization was by high-pressure (28 psig) air. A gas ring normally used for natural gas injection was found to be unstable with the particular flue-gas recirculation pattern used. Therefore a gas gun was used, rather than a ring, for most of the gas fuel tests.

The percentage reductions in NO_x and resulting changes in efficiency are shown in Table IV. The No. 2 oil results are unusual in that a [illegible]% NO_x reduction was achieved with flue gas recirculation alone. This may be because the high-intensity mixing and atomization by the air atomizer, and the relatively high volatility and low nitrogen content of the fuel, combined to give a gas-like flame.

The results for combined modification with No. 6 oil are also unusual in that NO_x reductions of 55% as shown have not been previously achieved with fuels of this type.

It was noted that boiler efficiency was reduced by flue-gas recirculation even though no increase in excess O_2 was necessary. This is because the average temperature the combustion produces is reduced, lowering the temperature-difference potential for heat transfer. The flow per unit area increases, tending to increase heat transfer, but the reduced temperature difference results in a greater offsetting tendency for reduced heat transfer.

The results were achieved with CO concentrations of less than 500 ppmV and particulates emissions of less than 0.10 lb/million Btu.

These results are of course for one particular boiler and are not necessarily indicative of what might be achievable on a boiler of different size or design.

COMBUSTION MODIFICATIONS AT LOCATION 38

The industrial boiler at location 38 was a single burner oil- and gas-fired watertube unit with combustion air preheating, rated at 20000 kg (45,000 lb) per hour steam flow. Tests were conducted at 89% load. Second-stage combustion air could be injected through any of 10 side fire air ports. Combustion air preheat temperature could be varied from about 338 to 450 K (150 to 350 °F).

Baseline emissions of NO_x were as follows:

Fuel	Air Preheat K (°F)	NO_x, ppm, 3% O_2
Natural Gas	411 (280)	170
No. 6 oil	408 (275)	270

The effect of excess air on NO$_x$ was evaluated for both natural gas and No. 6 oil firing. The effect of O$_2$ on NO$_x$ for natural gas exhibited a leveling trend above approximately 2-1/2% O$_2$. The maximum reduction, at 1.45% O$_2$ was approximately 10% less than the nominal condition. With No. 6 oil a similar trend was exhibited. The reduction was approximately 17% from the nominal condition of 2.9% O$_2$.

The effect of combustion air preheat temperature on NO$_x$ was evaluated and showed a considerable decrease in NO$_x$ with reduced windbox temperature for both fuels. The windbox temperature variation had a greater effect on NO$_x$ with natural gas firing than with No. 6 oil firing. Nominal values of NO$_x$ decreases were 7.2 ppm/10 K (4 ppm/10 °F) for natural gas and 4.5 ppm/10 K (2.5 ppm/10 °F) for No. 6 oil.

The effect of staged combustion air (SCA) on NO$_x$ emissions was evaluated by injecting second-stage air through various combinations of opposing ports at five locations ranging from 100 to more than 300 cm from the furnace front. The data for NO$_x$ versus SCA port location for oil fuel indicated that the most effective injection point is that most distant from the burner. The data for natural gas firing indicate a similar trend, except that the ports nearest the burner exhibited the same effectiveness as did the most distant ports. This may be due to the different geometric relationship between burner fuel and air flows (center oil gun vs. outside ring gas burner) and greater sensitivity of the NO emissions to combustion air temperature with natural gas. At the nominal condition of 2.8% O$_2$ and 14% SCA flow, the NO$_x$ was reduced 30% for No. 6 oil with injection at approximately 300 cm from the furnace front. Reducing the operating O$_2$ to 2.3% reduced the NO$_x$ by 42% from the baseline condition. Staged combustion with natural gas resulted in a reduction of 32% from the baseline condition with the boiler operating at 2.4% excess O$_2$ and 14% SCA.

SECTION 6

TRACE SPECIES AND ORGANIC MEASUREMENTS

INTRODUCTION

Measurement of trace species and organic emissions were made on seven of the devices tested in this program:

Device Type	Test Site No.	Fuel	Sample Position
Forced draft heater	12/2	Ref. gas	Furnace stack
Wet process cement kiln	9	Nat. gas	Precipitator inlet & outlet
Steel open hearth furnace	14	NG + No. 6 oil	Precipitator inlet
Black liquor recovery boiler	10/2	Liquor	Precipitator inlet & outlet
Wood bark boiler	13	Wood+coal	Precipitator outlet
Diesel engine	15	No. 2 oil	Engine stack
Modified boiler	19	No. 6 oil	Stack at baseline & low NO_x

The analysis of samples collected is not yet complete for these devices. However, an initial sampling system check run was conducted on a coal-fired boiler in the KVB laboratory. Results of that test are presented.

SAMPLING PROCEDURE

The EPA (IERL-RTP) has developed the Source Assessment Sampling System[1] (SASS) train for the collection of particulate and volatile inorganic and organic matter with a single sampling system. A stainless steel heated probe is connected to an oven module containing 3 cyclones and a filter. Particle size fractionation is accomplished in the cyclone portion of the SASS train, which incorporates the cyclones in series to provide large quantities of particulate matter size-classified into three ranges: a) >10 µm, b) 3 µm to 10 µm, and c) 1 µm to 3 µm. A fourth cut, <1 µm, is obtained with a standard 142 mm filter. Volatile organic material is collected in an organic sorbent module. The module is an integral part of the gas treatment system which follows the cyclone oven. The gas treatment system is composed of four primary components: a gas temperature conditioner, an organic adsorbent trap, the aqueous condensate collector, and a temperature controller. The organic sorbent is XAD-2 porous polymer resin with the capability of adsorbing a broad range of organic species. Volatile inorganic elements are collected in a series of three liquid impingers followed by one impinger containing a drying agent. The pumping capacity is supplied by a 10-cfm high volume vacuum pump. Required pressure, temperature, power and flow conditions are obtained from a main controller module.

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[1] Manufactured by Aerotherm Corporation, 485 Clyde Avenue, Mountain View, CA, 94042, Tele. (415) 964-3200.

Procedures for use of the SASS train as part of a complete environmental assessment test program have been detailed by EPA (Ref. 10). KVB used those procedures as the basic approach to sampling in the current program. However, the current program was not formulated as an environmental assessment as defined in Reference 10. Rather, the objective was to quantify the emissions and mass distribution characteristics of 24 specific inorganic species, total polycyclic organic matter (POM), eight specific POM compounds, and total polychlorinated biphenyls (PCB). In addition, the general nature of emissions of a large number of elements was to be examined. The specific list of species to be identified is presented later in this section in the discussion of sampling results.

The SASS train was used for sampling stack gases and samples were also collected of all the input and output materials such as fuels, process feed, products and wastes as necessary to establish mass distributions.

SAMPLE ANALYSIS

Sample analysis involved the use of atomic absorbtion, spark source mass spectrometry, and wet chemistry for inorganic species. POM and PCB were analysed by extraction with pentane, isolation by aliphatic-aromatic separation with pentane and benzene elution by silica gel adsorbtion chromatography. The benzene fraction was analysed for POM and PCB using gas chromatography employing combined flame ionization and electron capture detectors. This analysis is being performed by Calspan Corporation, Buffalo, NY.

For selected samples indicated to have high POM content, analysis by gas chromatography and mass spectrometry is being performed to more positively quantify POM content. This analysis is being performed by the Battelle-Columbus Laboratory.

LABORATORY BOILER SAMPLING TEST

Previous trace species and organic sampling by KVB with a modified EPA Method 5 sampling system had indicated deficiencies in collection of volatile inorganics (Ref.15). That sampling system was also very cumbersome for use on stack platforms. For the current program, it was deemed desirable to conduct a well-controlled laboratory test both to evaluate the sampling ability of the SASS system and field test compatibility. Such a test was conducted in a combustion research laboratory at KVB.

The KVB laboratory boiler is a scotch type dry back boiler with a rated heat input of 1.2 MW (4 x 10^6 Btu/hr). The boiler was fitted with a single burner for firing pulverized coal. Preheated air is supplied at 533 K (500 °F) by forced draft. The boiler exhaust is cleaned with a baghouse. Prior to the test, the boiler was disassembled and cleaned so that ash deposited during the test could be recovered. The SASS train sample point was located in the duct between the boiler and the baghouse.

The coal fuel was Pittsburg #8 West Virginia coal. Proximate and ultimate analysis as received was:

Proximate (% weight)	
Moisture	1.50
Volatile	37.89
Fixed Carbon	53.15
Ash	7.46
Sulfur	2.69
Heating value,	
kJ/kg	31827
(Btu/lb)	13684

Ultimate (% weight)	
Moisture	1.50
Carbon	76.28
Hydrogen	5.[illegible]
Nitrogen	1.49
Sulfur	2.69
Chlorine	0.04
Ash	7.46
Oxygen (diff)	5.45

This coal was recommended by EPA because the trace element content was known to be sufficiently high to enhance SASS train evaluation.

The test plan was established on the basis of a SASS train sample collection volume of 30 m^3 (1060 ft^3) as specified in Reference 10. The train used had a design sampling rate of 4.0 actual wet cubic feet per minute (0.00189 a w N m^3/S) through the cyclone train at 478 K (400 °F) or 0.00111 dry N m^3/S (2.34 std ft^3/m) at standard dry conditions. Sample time to collect 30 dry N m^3 was 7.54 hours. (The SASS train has since been redesigned for a higher flow rate of 0.00189 std N m^3/S (4.0 std ft^3/m)).

The test conditions are summarized in Table V. Total boiler operating time was 16.7 hours (continuous) of which 7.53 hours were required (intermittently) for sampling. The additional 9.2 hours was required to resolve train operational problems and to change the filters and dryerite in the train. Three filters were used. The quantity of ash removed from the furnace was 91% (carbon and moisture free) of the expected ash based on coal analysis. Train operation was very stable. The isokinetic sampling rate varied from 82% to 106% with an average of 100.6%.

Conclusions from the test regarding operational capability of the SASS train were:

1. The train functioned properly throughout the test with respect to sample acquisition capability.
2. Mechanical problems with the cyclone assembly were experienced and attributed to the type of connecting fittings used. The fittings were not well suited for repeated use since deformation of mating surfaces (rendering separation difficult) is not easily avoided when a leak-free joint is desired. The threaded parts also galled at elevated temperatures because no lubricants could be used to avoid contamination.
3. Ice consumption in the impinger bath was excessive, 122 kg (270 lb) were used. Insulating the ice bath from surrounding air may help to maximize its cooling effectiveness.
4. No condensation occurred in the XAD-2 module operated at 328 K (130 °F). This temperature is above the dew-point for coal fuel exhaust (IERL-RTP has specified

lower temperature for future tests). The XAD-2 module satisfactorily maintained the adsorbent temperature within 3 °K (5 °F) of the desired temperature.

5. Boiler ash recovered was close to 100% of expected ash. SASS train particulate catch was within 20% of expected collection. These results should provide a good basis for mass balance of the trace elements.
6. Pluggage of the sampling filter necessitated renewal of the filter element two times during the test. Particulate grain loadings were similar to those encountered upstream of particulate removal devices at conventional pulverized coal fired boilers. To minimize downtime for filter changes, a large filter design may be necessary to allow a 4 to 5 hour run period per filter.

RESULTS OF SAMPLE ANALYSIS

Samples were analyzed for the species listed in Table VI. Results expressed as mass flow rates are indicated for the coal, ash retained in the furnace, SASS train samples, and the baghouse ash.

Coal samples were taken at approximately one-half hour intervals during that entire test period. Two composite coal samples were analyzed: one consisted of equal portions from the entire amount of coal burned and the second consisted of equal portions of only that coal burned during actual sampling by the SASS train. The species input rates for both coal samples are similar with the exception of antimony, cadmium, fluoride, and total POM. These four species were lower in the coal burned during SASS sampling. Five species were below detection limits in both coals: selenium, tellurium, tin, nitrates, and total PCB. Only tellurium and total PCB were below detection limits for all collected samples.

Most of the elements with non-volatile characteristics were collected in the solids section of the SASS train. Antimony and arsenic were expected to be collected mainly in the impingers; however, larger amounts were collected in the solids section. Mercury was predominantly collected by the impingers as expected and most total POM was collected in the organic module as expected. Results for all PCB measurements on every sample analyzed were all below detection limits. The collection of chromium and nickel was unexpectedly high in the organic module, attributed to erosion of stainless steel from the train. With the exception of tellurium and total PCB, every species was above detection limits for the total amount collected by the SASS train.

Mass balances on each specie were evaluated and several criteria for performance evaluation are presented in Table VII. The first column lists the specie stack emission rate in $\mu g/m^3$ as measured by the SASS train. The amount of each species input by the coal less the amount retained in the furnace ash is a measure of the potential emission rate assuming all unretained species are emitted in the stack. In calculating the unretained amount, the furnace ash amount was subtracted from the amount input by the total amount of coal burned. The resulting difference was then multiplied by the ratio of the amount measured in the coal burned only during the SASS sampling period to the amount measured in the total coal. This result was then used as the unretained amount for comparison with the amount collected by the SASS train. This procedure corrects for differences in the coal sampler.

The second column in Table VII gives the ratio of amount collected by the SASS train to the unretained amount. For six elements, (antimony, barium, cadmium, calcium, cobalt and titanium), the relative emission ratios are within + 14% - 7%. Barium, calcium, and titanium are elements that are most likely to produce a good mass balance because of low volatility and absence of contamination. The excellent mass balance on these elements therefore verifies the basic acceptability of the test procedures and sample handling. There are four elements with negative values (chromium, manganese, nickel and zinc), indicating a larger amount was found in the furnace ash than was input from the coal. These four elements are those for which the coal input could be augmented by metal in the train or boiler. It is therefore difficult to evaluate the train collection mass balance performance on these elements. Four species (arsenic, copper, tin, and chloride) have large positive values, indicating much higher SASS collection rates compared with the unretained emission. Iron is also higher by a factor of two. Elements for which the relative emission ratio was low include beryllium, lead, and selenium. Total POM is also very low, but this is expected because POM in the coal should be consumed in the flame. The results indicate about 98% of the POM is burned and 2% is emitted. For vanadium and mercury the relative emission ratio is low.

The third column in Table VII lists the ratio of amounts collected in the cyclone and filter section of the SASS train to that collected in the baghouse. The SASS train should be a better collection device compared to the baghouse so that all ratios would be expected to be greater than unity. The values in the table that are significantly less than unity include those for calcium, selenium, zinc, and fluoride. The ratios for antimony and arsenic are substantially greater than unity indicating that the SASS cyclones are collecting unexpectedly high amounts of these two volatile elements.

The fourth column in Table VII lists the overall mass balance for each species. The trends are similar to those of the relative emission ratio but a value of close to one for the mass balance can be misleading in judging SASS train performance in those cases where most of the species is retained in the furnace. In general, the overall mass balances were within a factor of 2 to 3 which is the stated objective for initial environmental assessment tests (Ref. 10). However, values for chromium, nickel, selenium, and chloride exceed a factor of three.

The last column in Table VII lists mass balance values based on the baghouse collection instead of the SASS train. These values are of use in assessing whether the mass balance errors are the result of poor train collection efficiency or are the result of experimental uncertainties.

Conclusions

The excellent mass balances obtained on the major non-volatile elements verified the basic test procedures, sample recovery, and analysis. The fact that the major portion of the organics was collected in the organic module and that organics downstream of the module (impingers) were below detection limits verified that no organic breakthrough occurred and that organic collection efficiency was excellent. Results for collection of the most volatile elements, antimony, arsenic, mercury and selenium were mixed. The amounts of antimony and arsenic collected exceeded expected levels based on mass balances and collection in the solids section was higher than expected. Only about 50%

of the mercury was recovered. Selenium recovery was only about 25%. However, the concentrations in the coal of mercury (0.03 µg/g) and selenium (1 µg/g) were very low and further analysis of the experimental precision is necessary to evaluate the results.

The results of this laboratory test will be of importance in evaluating results obtained in field tests on this and other programs.

SECTION 7

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TABLE 1. RANKING OF MAJOR NO$_x$ STATIONARY SOURCES ACCORDING TO THREE DATA SETS

No.	Source	NO$_x$ Gg/y[1] (Ref. 6)	NO$_x$ Gg/y (Ref. 7)	NO$_x$ Gg/y (Ref. 8)
1	Boilers, Utility, Coal	3495	3660	4200
2	Engines, Reciprocating	2132	1945	245
3	Boilers, Ind/Coml, Oil	1245	1040	363
4	Boilers, Utility, Oil	1114	765	955
5	Boilers, Utility, Gas	835	860	1010
6	Boilers, Ind/Coml, Coal	735	561	513
7	Boilers, Ind/Coml, Gas	491	467	712
8	Gas Turbines	253	236	87
9	*Heaters, Petroleum Process	167	--	880
10	*Kilns, Cement	91	99	130
11	Space Heating, Ind/Coml	81	--	--
12	*Furnaces, Glass	68	116	5
13	Catalytic Cracking, Petroleum	61	47	36
14	*Furnaces and Smelters, Metals	--	--	40
15	Coal Refuse Piles (and Mines)	31	--	--
16	Nitric Acid Mfg	27	127	78
17	*Wood Waste Incin., Boilers	24	--	137
18	*Kilns and Dryers, Brick	9	--	2
19	*Mineral Wool Mfg	8	--	0
	Others	504	2363	1360
	Total	11371	12306	10753
	Major Group Totals			
	Boilers (coal, oil gas)	7915	7373	7753
	Engines, Reciprocating	2132	1945	239
	Gas Turbines	253	236	87
	*Industrial Combustion	350	215	1154

[1] 1 Gg/y = 1100 tons/yr

TABLE 11. INDUSTRIAL COMBUSTION TEST UNITS SELECTED AND SUMMARY OF RESULTS OBTAINED

Device Type	Test Site No.	Fuel	Average Baseline NO_x ng/J[1]	ppm @ 3% O_2	Maximum Percent Reduction in NO_x	Combustion Modification[2]
Natural Draft Process Heater	4	Ref.Gas	59	116	10	4/12 BOOS
Natural Draft Process Heater	5/1	Ref.Gas	50	97	22	Air Register Adjust
Natural Draft Process Heater	5/2	Ref.Gas	39	76	21	High Load; Low O_2
Natural Draft Process Heater	7/1	Ref.Gas	52	103	8	2/16 BOOS
Natural Draft Process Heater	7/2	Ref.Gas	49	98	24	Air Register Adjust
Forced Draft Heater; Air Preheat	12/1	Ref.Gas	163	320	0	Baseline Lowest O_2
	12/1	No.6 Oil	113	222	0	Low O_2 No Effect
Forced Draft Heater	12/2	Ref.Gas	109	214	67	Low O_2
	12/2	No.6 Oil	80	157	8	Low O_2
Clay Tunnel Kiln	1	Nat.Gas	46	90	41	Low O_2
Rotary Cement Kiln (Dry Process)	3	Nat.Gas Oil/Coke	1425	2300	50	Fuel Switch; Gas to Coke
Rotary Cement Kiln (Wet Process)	9	Nat.Gas	1319	2250	14	Low O_2; High Air Temp.
Steel Open Hearth Furnace	14	NG + No.6 Oil	1094	2070 (Avg)	40	Low O_2
Steel Reheat Furnace	16/1	Nat.Gas	56	110	43	3/27 BOOS
Steel Soaking Pit	16/2	Nat.Gas	52	101	69	Low O_2
Aluminum Melter	5	Nat.Gas	49	96	0	Low O_2 (NO_x increased)
	6	No.2 Oil	104	185	0	Low O_2 (NO_x increased)
Black Liquor Recovery Boiler	10/3	Liquor	--	52	30	Secondary Air Adjust
Wood Bark Boiler	10/1	Wood+NG	124	229	40	Low O_2
Wood Bark Boiler	13	Wood+Coal	108	300	15	Low O_2
CO Boiler	11	CO Gas	65	126	[illegible]	Low O_2
Natural Gas Engine	2	Nat.Gas	1020	1996	20	Fuel; Air Adjust
Diesel Engine	15	No.2 Oil	830	1476	7	Low Inlet Air Temp.
Gas Turbine Combined Cycle	7/3	Ref.Gas	59	119	14	1/8 BOOS
Gas Turbine Combined Cycle	8	Ref.Gas	52	103	30	3/16 BOOS

[1] 1 lb/10^6 Btu = 430 ng/J

[2] BOOS = Burners out of service

TABLE III. SUMMARY OF EMISSION MEASUREMENT INSTRUMENTATION

Emission Parameter	Symbol	Measurement Method	Equipment Manufacturer
Nitric oxide	NO	Chemiluminescent	Thermo Electron
Oxides of nitrogen	NO_x	Chemiluminescent	Thermo Electron
Carbon monoxide	CO	Nondispersive infrared	Beckman
Carbon dioxide	CO_2	Nondispersive infrared	Beckman
Oxygen	O_2	Polarographic	Teledyne
Hydrocarbons	HC	Flame ionization	Beckman
Sulfur dioxide	SO_2	UV spectrometry	Du Pont
Sulfur dioxide Sulfur trioxide	SO_2 SO_3	Absorption/titration	Shell-Emeryville Absorption train
Total particulate matter		EPA Std. Method 5	Joy Mfg. Co.
Particulate size distribution		Cascade impactor, electro-balance	Anderson, Brink, Cahn
Smoke spot		Field service type smoke tester ASTM D-2156	
Opacity		EPA Std. Method 9	
Trace species and organics	TS&O	Source Assessment Sampling System (SASS)	Aerotherm

TABLE IV. SUMMARY OF NO_x REDUCTION AND EFFICIENCY CHANGE AS A FUNCTION OF COMBUSTION MODIFICATION TECHNIQUE FOR VARIOUS FUELS
LOCATION 19

	Natural Gas		No. 2 Oil	No. 6 Oil
	Ring	Gun	(0.00% N)	(0.20% N)
Baseline NO_x, ppmV at 3% O_2	96	92	110	221
Combustion Modification Technique	NO_x Reduction, Percent of Baseline			
Lowered O_2	19[1]	3.3	20	30
Staged Combustion Air (SCA), Normal O_2	32	46	30	29
SCA, Low O_2	42	--	44	42
Flue Gas Recirculation (FGR), Normal O_2	--	77	58	11
FGR, Low O_2	--	79	73	40
FGR + SCA, Normal O_2	--	76	69	53
FGR + SCA, Low O_2	--	[2]	77	55
Baseline efficiency	78.2	82.6	82.5	82.5
Combustion Modification Technique	Change in Efficiency, Percent			
Lowered O_2	-1.2[1]	+0.9	+1.5	+1.5
SCA, Normal O_2	+0.1	+0.3	+0.9	+0.1
SCA, Low O_2	+0.5	--	+1.1	+0.8
FGR, Normal O_2	--	-0.8	-1.9	-0.7
FGR, Low O_2	--	-0.4	+0.9	+0.6
FGR + SCA, Normal O_2	--	-0.5	-1.2	-0.8
FGR + SCA, Low O_2	--	[2]	-0.8	+0.1

[1] NO_x reduction occurred at increased O_2 level.

[2] Stability limit prevented lowering O_2.

TABLE V. KVB BOILER SASS TEST SAMPLING CONDITIONS

	Total Boiler Operation Period	SASS Train Sampling Period
Operating time, min (h)	1002 (16.7)	452 (7.53)
Boiler firing rate, MW (10^6 Btu/h)	0.81 (2.8)	0.85 (2.9)
Coal burned, kg (lb)	1558 (3427)	721 (1586)
Ash collected, kg (lb)		
Furnace tube	51.4 (113)	
Firetubes	25.9 (57)	
Stack surface	1.4 (3)	
Baghouse	41.8 (92)	
Total	120.5 (265)	
Stack conditions (average)		
Velocity m/s (ft/s), diam = .28m		12.7 (41.7)
Flow rate N m^3/s (SCFM), wet		0.358 (760)
Flow rate N m^3/s (SCFM), dry		0.3404 (721)
Gas temperature, K (°F)		629 (673)
Excess oxygen, % dry		6.0
Moisture, %		5.0
Total gas volume, m^3 (ft^3) dry		9232 (326038)
SASS train conditions		
Actual cyclone flow rate, a m^3/s (ACFM), wet		0.00189 (4.0) ±10%
Flow rate, standard, dry, N m^3/s (SCFM)		0.00111 (2.34)
Total meter volume, m^3 (ft^3), dry		33.4 (1180)
Total standard volume, m^3 (ft^3), dry		30.0 (1060)
Oven temperature, K (°F)		478±2 (400±5)
XAD-2 module temperature, K (°F)		328±2 (130±5)
Isokinetic rate, %		100.6
Solid particulate collected, g		77.07
Solid particulate loading, g/DSCM (gr/DSCF)		2.6 (1.12)
Emission factor, ng/J (lb/MMBtu)		957 (2.23)

TABLE VI. KVB BOILER SASS TEST SAMPLE MASS FLOW RATES.

TABLE VII. KVB BOILER SASS TEST EMISSION MASS BALANCE

Species	Emission[1] by SASS ($\mu g/m^3$)	Relative[2] Emission Ratio	Solids[3] Ratio, SASS:BAG	SASS[4] Mass Balance	Baghouse[5] Mass Balance
Antimony	690	1.18	1000.1	0.88	1.001
Arsenic	111-170	5.40	4.0	1.31	0.37
Barium	1900	0.47	1.5	0.80	0.95
Beryllium	13-16	0.20	0.50	0.41	0.34
Cadmium	8-118	1.12	0.52	1.13	1.00
Calcium	11000	0.91	0.44	1.51	1.06
Chromium	4500	111.52	1.10	8.15	1.05
Cobalt	140	1.98	1.40	1.31	0.15
Copper	190	17.52	3.11	1.69	1.50
Iron	180000	1.20	1.19	1.11	1.04
Lead	110	0.29	1.00	0.41	0.19
Manganese	730	4.13	1.50	1.13	1.49
Mercury	1.1-1.7	0.53	1.15	0.04	0.18
Nickel	1600	4.11	0.01	0.11	2.14
Selenium	3.1-4.0	0.13	0.51	0.13	0.13
Tellurium	<130	DL	DL	DL	DL
Tin	125-670	1.07	0.04	1.30	1.28
Titanium	1030	1.00	1.15	1.09	0.95
Vanadium	640	0.48	1.00	0.61	0.53
Zinc	415	11.70	0.25	1.23	1.40
Chloride	84000	51.10	1.27	84.30	0.56
Fluoride	1100	3.10	10.08	1.00	0.90
Nitrates	2800	DL	DL	DL	DL
Sulfates	64000	0.14	2.23	0.38	0.31
Total POM	220-280	0.02	17	0.02	1.002
Total PCB	<131	DL	DL	DL	DL

NOTES: [1]SASS Emission = (collected sample mass; µg)/(sample volume; m³)

[2]Relative Emission Ratio = (SASS emission; µg/m³) x (stack flow; m³/s)/(coal input; µg/s × ash retention; µg/s)

[3]Solids Ratio, SASS:BAG = (SASS solids emission rate; µg/s)/(baghouse collection rate; µg/s)

[4]SASS Mass Balance = (ash deposition rate; µg/s + SASS emission rate; µg/s)/(coal input; µg/s)

[5]Baghouse Mass Balance = (ash deposition rate; µg/s + baghouse collection rate; µg/s)/(coal input µg/s)

DL = Measurement below detection limits

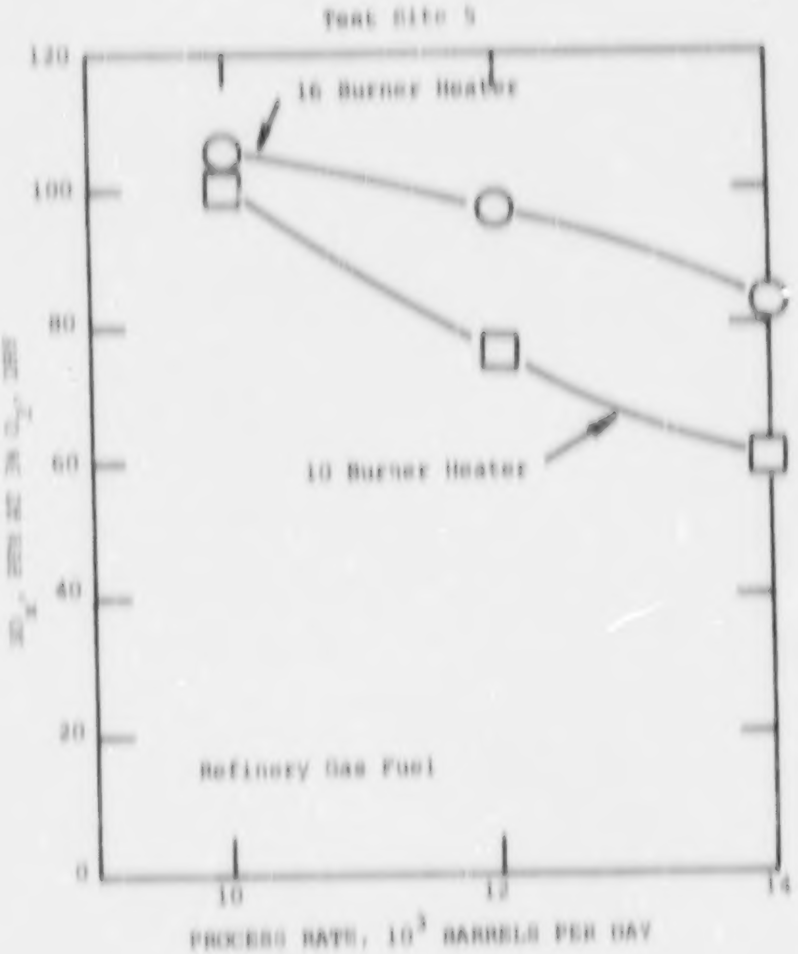
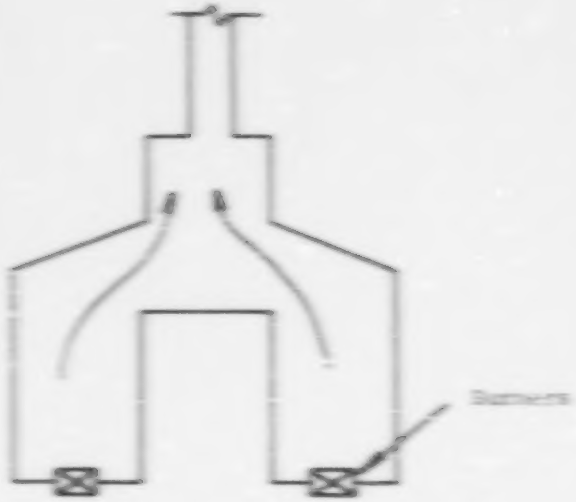


Figure 1. Effect of process rate on NO_x emissions from a process heater.



Test Site 4 Refinery Gas

LEGEND

	FUEL	REGISTER
○	ON	Full Open
●	OFF	Closed
⊠	OFF	Full Open
◓	ON	Part Open

BURNER PATTERNS	CONDITION	NO_x PPM AT 3% O_2	EXCESS O_2, %
●○○○○○○○○○○○○○○●	Baseline	116	4.7
⊠○⊠○○○○○○○○○○⊠○⊠	Pattern 4-7	113	5.0
⊠◓⊠◓◓◓◓◓◓◓◓◓◓⊠◓⊠	Pattern 4-7A	105	5.4
◓◓◓⊠◓◓⊠◓◓⊠◓◓⊠◓◓◓	Pattern 4-9	95	4.8
◓◓◓⊠◓◓◓⊠⊠◓◓◓⊠◓◓◓	Pattern 4-10	103	5.1
◓◓◓◓◓⊠◓⊠⊠◓⊠◓◓◓◓◓	Pattern 4-11	107	5.0

Figure 1. Staged combustion by removal of burners from service on a process heater.

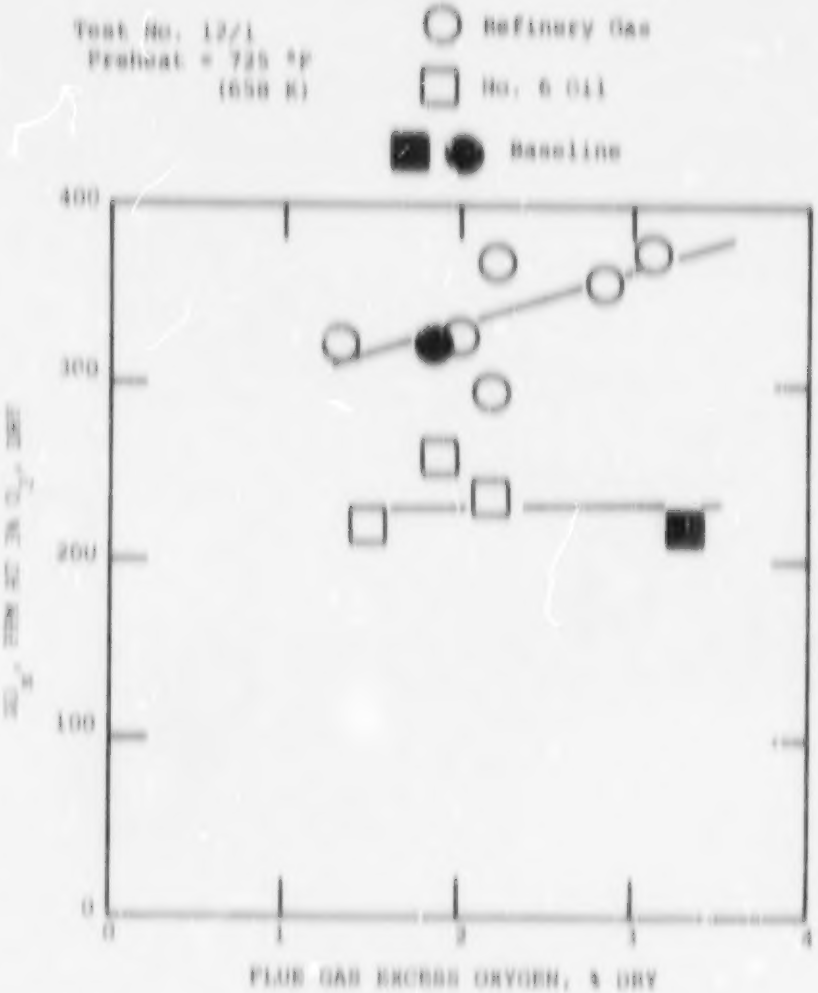


Figure 1. NO_x versus excess O_2 for a balanced draft process heater with combustion air preheat.

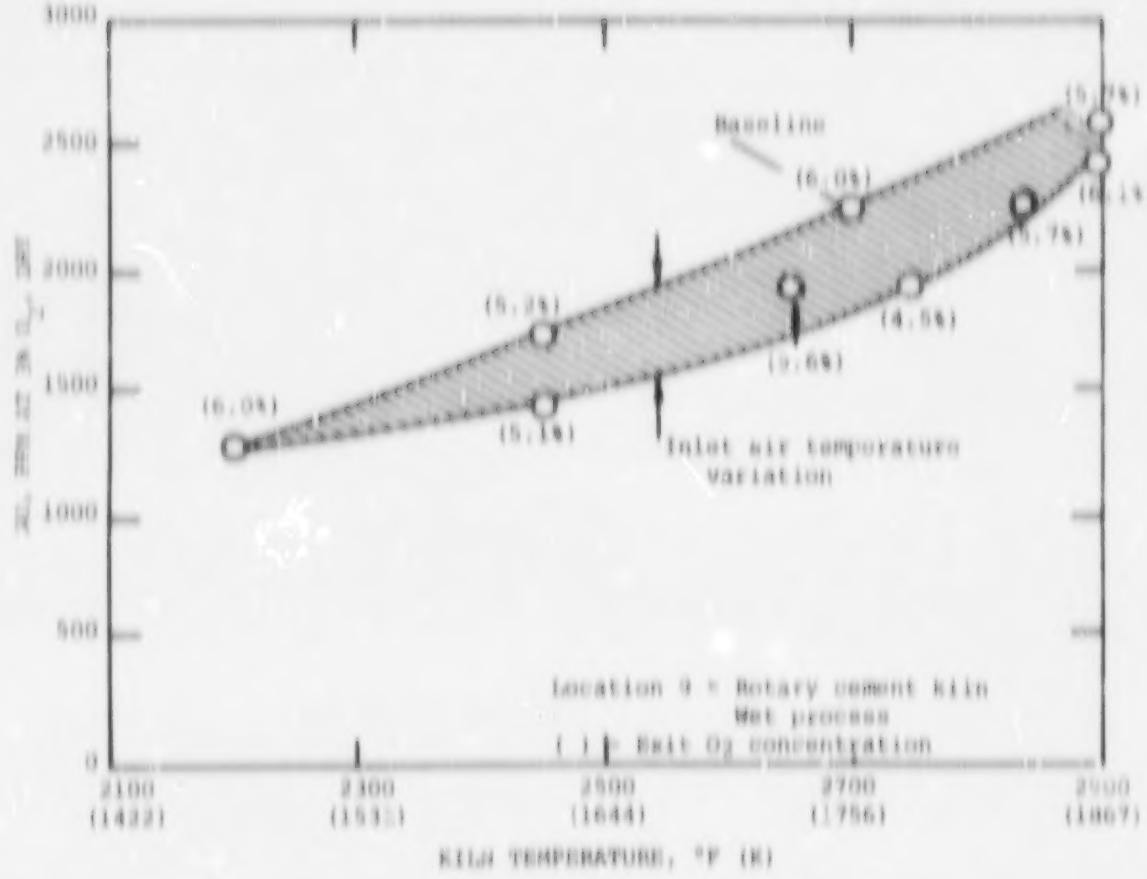


Figure 4. The effect of cement kiln temperature on NO emissions.

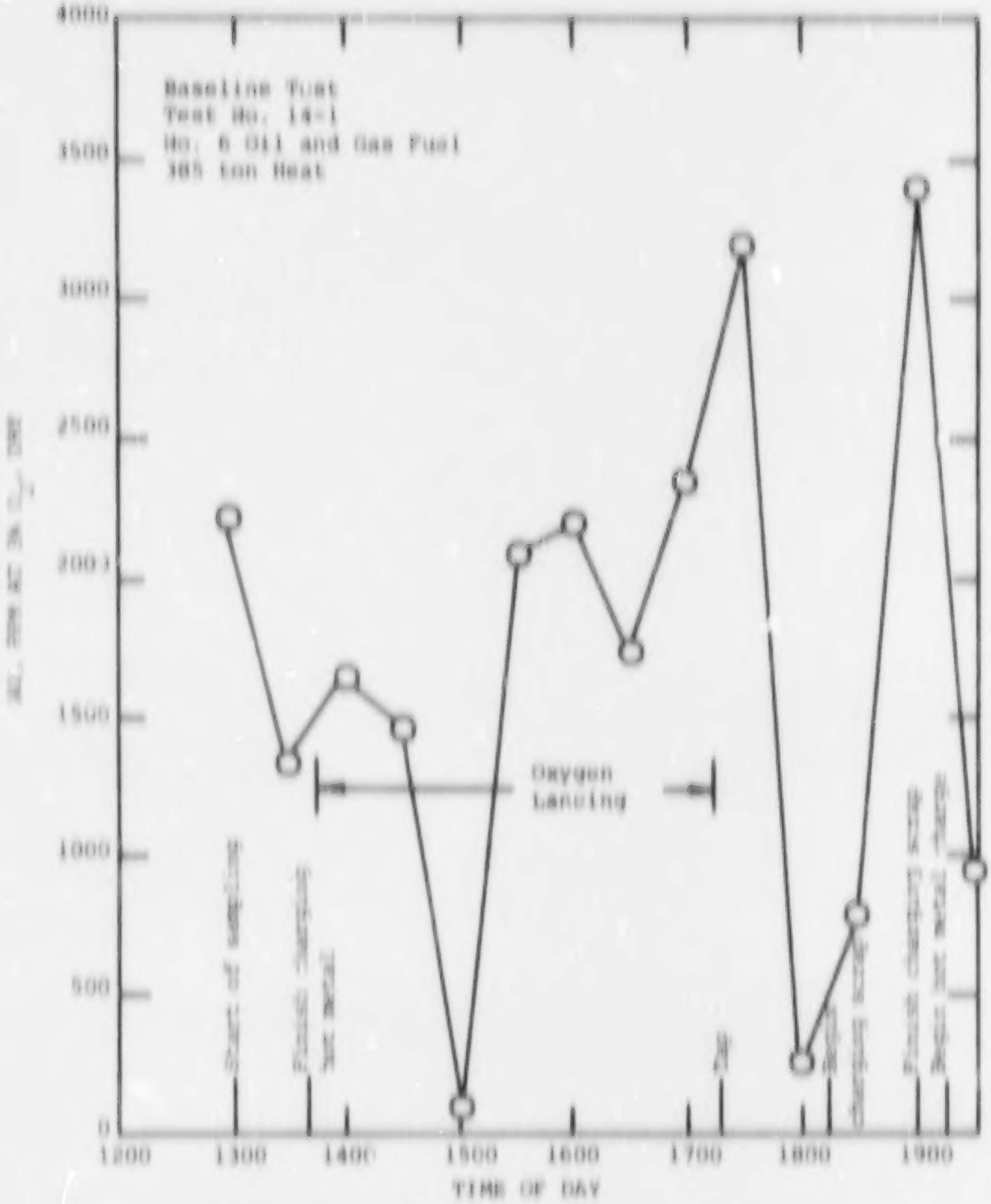


Figure 5. NO emissions as a function of time for an open hearth furnace.

BOILER BURNER DESIGN CRITERIA FOR RETROFIT WITH LOW-Btu GASES

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ABSTRACT

This research program was initiated to characterize the problems associated with retrofitting existing utility boilers with low-Btu gases manufactured from commercially available coal conversion processes. All the experimental results were gathered from a pilot-scale furnace fired with a movable-vane boiler burner at a rate of 2,250,000 Btu/hr. Low-Btu gases tested ranged in heating value from 300 Btu/SCF to 100 Btu/SCF and were synthetically produced with a natural gas reformer-generating system.

Data were collected to permit a comparison between natural gas and low-Btu gases in the areas of flame stability, flame length, flame emissivity, changes in boiler efficiency, and NO_x emissions. The NO emission data yielded an activation energy of 153 kcal/mol compared to kinetic models which predict 135 kcal/mol. This good agreement suggests that peak temperatures approaching the adabatic flame temperature are controlling the rate of NO emissions. Thus, the use of the adabatic flame temperature provides a good empirical method for predicting NO emissions from low-Btu gas combustion.

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INTRODUCTION

The electric power industry is caught between the Federal Government's concern for cleaning up the environment and for decreasing (or eliminating) our dependence on foreign sources for oil. The environmental concerns make the use of coal prohibitively expensive, if not impossible, because of the necessity of decreasing sulfur emissions. Low-sulfur oil could replace coal, but this oil must be imported, which is against long-range government policy. Coal appears to be the only fossil fuel available in sufficient quantities to eliminate the necessity of importing oil; however, an environmentally acceptable and practical way must be found for its use.

One concept that could provide a practical method for using coal is to convert it to low-sulfur, ashless, low-Btu gas for use in boilers. This would alleviate both the utility industry's fuel supply problem and the air pollution problem. Of particular concern, however, are the prospects of operating problems and loss of boiler output (downrating), which can occur when retrofitting a unit originally designed to use another fuel. Accurate combustion data are needed to define the potential magnitude of these problems and to indicate whether practical solutions are possible.

This paper presents results from an experimental program designed to characterize the problems associated with retrofitting existing boilers for low- and medium-Btu gases made from commercially available coal conversion processes. Data were collected to permit a comparison of natural gas and low- and medium-Btu gases in the areas of:

- Flame stability
- Flame length
- Flame emissivity
- Flue-gas pollutant emissions, and
- Boiler efficiency

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SUMMARY

All of the experimental results presented in this report were taken from a pilot-scale furnace fired with a movable-vane boiler burner (MVBB) at a heat input of 2.25 million Btu/hr.* In addition to natural gas, five medium- and low-Btu gases were tested: Lurgi oxygen, Koppers-Totzek oxygen, Winkler oxygen, Wellman-Galusha air, and Winkler air. A synopsis of the test results for a 45-degree vane angle is presented in Table 1. This table includes furnace operating conditions, burner operating conditions, fuel combustion properties, and experimental data for the MVBB with a 45-degree vane angle. The information includes gross heating value of the fuel; adiabatic flame temperature with 3% excess oxygen and combustion air preheat of 125°F; input velocity of fuel and combustion air at 60°F; hydrogen-to-carbon monoxide ratio of fuel; gross input enthalpy, including combustion air preheat; chemical species analysis of flue gases; volume of flue gases at 60°F; measured flue-gas temperature; measured furnace rear-wall temperature; calculated and measured emissivity; and concentration of NO measured in the flue at 3% excess oxygen.

Based on a detailed analysis of the experimental data, the following conclusions were made:

1. Flame stability was established for each test fuel under the most severe operating conditions, that is, with the furnace walls, burner block, and combustion air at ambient temperature. The flame stability was very sensitive to fuel jet velocity leaving the fuel nozzle. An injection velocity of 100 ft/s was found to give the best operation.

2. For all fuel gases tested, the flame length decreased with increasing movable-vane angle (swirl of the combustion air). Medium- and low-Btu fuel gas flames were shorter than those for natural gas with the exception of Winkler air at a 45-degree vane angle, which produced a flame 10% longer than the natural gas flame.

3. Babcock and Wilcox used the pilot-scale test furnace data as input to their utility boiler design calculation to evaluate overall unit output when retrofit with medium- and low-Btu gases. The calculation technique used divided the boiler into a radiant (furnace) section and a convective section. The IGT experimental data were used as input conditions to the convective section. The

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* It is EPA policy to use metric units; however, in this report English units are occasionally used for convenience. See attached conversion table.

Table 1. SYNOPSIS OF FURNACE OPERATING CONDITIONS (Part 1)

Fuel	Gross heating value, Btu/SCF	Adiabatic flame temp, °F	H_2/CO ratio	Fuel input vel, ft/s	Combustion air inlet vel, ft/s
Natural gas	1035.0	3517	—	100.6	53.3
Lurgi oxygen	285.4	3164	2.2	100.0	51.2
Winkler oxygen	270.2	3329	1.3	105.6	52.3
Koppers-Totzek oxygen	285.0	3570	0.7	97.6	56.4
Wellman-Galusha air	139.4	2988	0.5	136.4	56.6
Winkler air	116.3	2579	0.6	109.6	74.7

Table 1. SYNPOSIS OF FURNACE OPERATING CONDITIONS (Part 2)

Fuel	Gross heat input, Btu/hr	Flue products N_2 %	CO_2 %	H_2O %	O_2 %	Vol of flue products, CFH at 80°F	SCF air / SCF fuel	SCF flue products / SCF fuel
Natural gas	2,371,265	72.5	8.3	16.7	2.5	27,357	11.23	12.26
Lurgi oxygen	2,336,066	62.9	16.8	17.8	2.5	27,565	2.71	3.41
Winkler oxygen	2,330,940	63.1	18.3	16.1	2.5	26,169	2.43	3.06
Koppers-Totzek oxygen	2,348,367	65.0	20.2	12.2	2.6	24,356	2.51	3.07
Wellman-Galusha air	2,358,036	72.3	15.8	9.2	2.7	32,772	1.34	2.33
Winkler air	2,338,940	74.5	14.6	8.2	2.8	38,339	1.13	1.96

Table 1. SYNPOSIS OF FURNACE OPERATING CONDITIONS (Part 3)

Fuel	Flue gas temp, °F	Rear wall temp, °F	Emissivity Calc	Emissivity Meas	Flue NO, ppm
Natural gas	2553	2309	0.159	0.177	65
Lurgi oxygen	2447	2300	0.194	0.185	32
Winkler oxygen	2523	2309	0.189	0.218	73
Koppers-Totzek oxygen	2554	2337	0.174	0.190	104
Wellman-Galusha air	2434	2066	0.154	0.190	13
Winkler air	2335	2012	0.150	0.170	4

design of the computer program did not allow information from the IGT tests to be inputs for the radiant section, although a comparison between the IGT experiment results and Babcock and Wilcox's predictions was made. The IGT data were used as input conditions to the convective section. It was found that all fuel gases tested were capable of maintaining boiler output; however, those with a heating value below 200 Btu/SCF may require retubing in the convective sections.

4. A second evaluation of furnace efficiency — defined for the purposes of this report as the fraction of the total enthalpy input to the furnace that is transferred to the furnace load — was made by Babcock and Wilcox using their standard design calculation technique. The inputs required for this calculation were: 1) fuel composition and 2) desired temperature of combustion products leaving the air heater. The values calculated for the combustion products of the fuel gases tested leaving the radiant section of the boiler agreed remarkably well with experimental values.

5. The furnace efficiency (fraction of heat transferred within the furnace) calculated with the well stirred model was found to be rather insensitive to emissivity, with a 10% change in emissivity producing only a 3% change in efficiency.

6. NO concentration levels from the medium- and low-Btu gases were ordered by adiabatic flame temperature. Only test fuels with heating values below 200 Btu/SCF had emission levels that conformed to the New Source Performance Standard.

7. The NO emission data yielded an activation energy of 153 kcal/mol compared to kinetic models which predict 135 kcal/mol. This good agreement suggests that peak temperatures approaching the adiabatic flame temperature are controlling the rate of NO formation. Also, the use of the adiabatic flame temperature provides a good empirical method of predicting NO emmissions.

PROCESS GASES SELECTED FOR STUDY

To ensure the immediate relevance of the program's results, only gas compositions from commercially available coal conversion processes (Lurgi, Koppers-Totzek, Winkler, and Wellman-Galusha) were considered. The gas properties of interest were heating value and hydrogen-to-carbon monoxide ratio (H_2/CO). To permit the study of a complete range of heating values and hydrogen-to-carbon monoxide ratios five gases were selected for testing. These five gases are listed below in Table 2, and a detailed gas composition analysis for each is given in Table 3.

Table 2. GASES SELECTED FOR TESTING

Test gas	Heating value, Btu/SCF (wet)	H_2/CO
Lurgi oxygen	285	2.2
Winkler oxygen	269	1.3
Koppers-Totzek oxygen	284	0.6
Wellman-Galusha air	160	0.5
Winkler air	117	0.6

These representative medium- and low-Btu gases are produced using the gas-generating and fuel-preparation facility shown schematically in Figure 1. The critical item in the gas supply system is the reformer, shown in Figure 2. This is a special gas generator that produces varying ratios of H_2/CO. Natural gas and carbon dioxide are fed to the reformer through a specially designed mixing tee. Additionally, steam may also be mixed, depending on the desired H_2/CO ratio. The resulting mixture is supplied to four reaction retorts contained in a vertical cylindrical furnace. The catalyst-filled retorts are heated by the furnace, and the input gases undergo endothermic chemical reactions at a temperature of 2100°F as they pass through the retort tubes. Globally, the reaction scheme is the water-gas shift. The gas generated within the reaction tubes passes through water-jacketed coolers, where it is quenched to prevent deterioration of the H_2/CO ratio.

The reformed gas is compressed to 30 psig and pushed through an MEA (methyl-ethyl-amine)-CO_2 (carbon dioxide) absorbing tower. This tower is used to remove CO_2 from the reformed gas if its concentration is above what is needed to synthesize the desired low-Btu gas. The reformed gas then enters a mixing chamber where it is blended with nitrogen, carbon dioxide, steam, and natural gas to reach the desired mixture of gas to be modeled. The product gas is analyzed by a gas chromatograph to ensure that the correct composition is attained. The synthesized gas is then fed to the pilot-scale furnace for combustion testing.

Table 3. SPECIES CONCENTRATIONS, ADIABATIC FLAME TEMPERATURES, AND GROSS HEATING VALUE (Wet) FOR MEDIUM- AND LOW-Btu GASES TESTED

Fuel	CO	H_2	CO_2	CH_4	N_2	H_2O	Adiabatic flame temp, °F	Heating value, Btu/SCF
Lurgi oxygen	18.5	40.2	29.4	9.4	0.6	1.9	3156	283
Winkler oxygen	32.9	41.2	20.0	3.0	1.0	1.9	3327	269
Koppers-Totzek oxygen	57.1	30.5	9.2	0.3	1.0	1.9	3578	284
Wellman-Galusha air	26.3	14.3	7.4	2.6	46.9	1.9	2948	160
Winkler air	21.1	13.0	6.9	0.6	56.5	1.9	2579	116

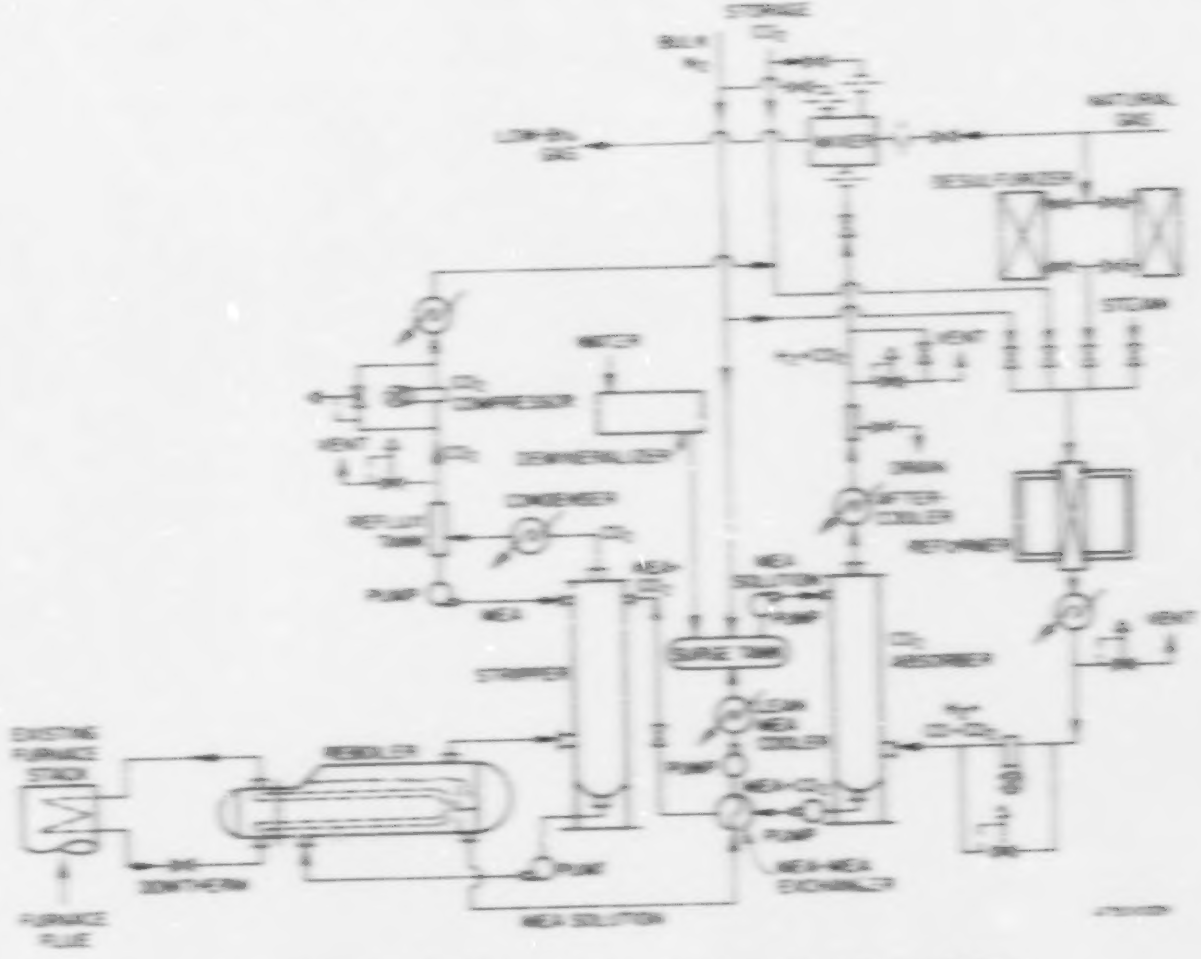
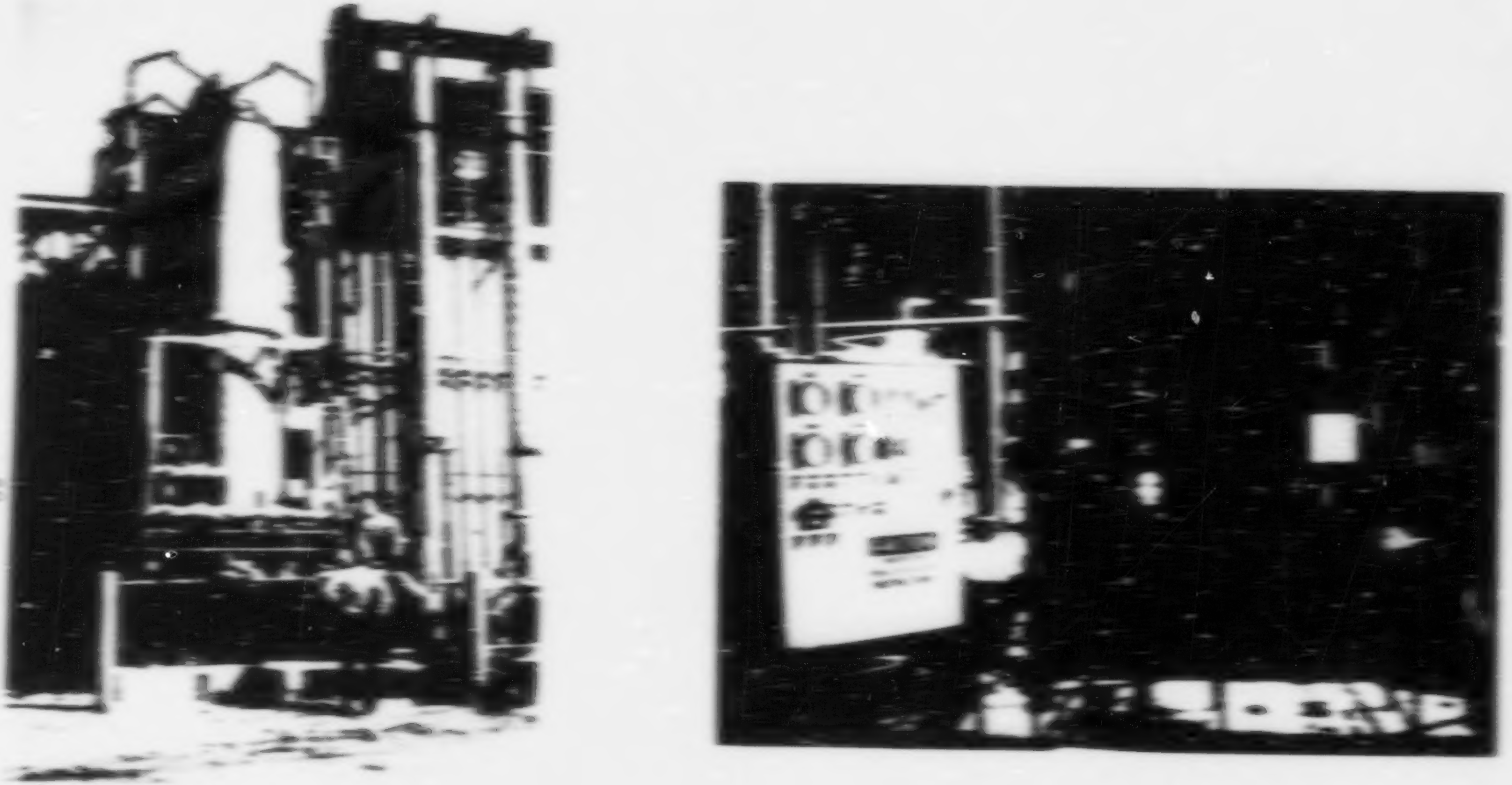

STORAGE CO_2
BULK N_2
NATURAL GAS
LOW-O_2 GAS
MIXER
DESULFURIZER
STEAM
VENT
WATER
CO_2 COMPRESSOR
DEMINERALIZER
VENT
DRAIN
AFTER-COOLER
REFLUX TANK
CONDENSER
CO_2
REFORMER
PUMP
MEA
MEA + CO_2
MEA SOLUTION
PUMP
VENT
SURGE TANK
STRIPPER
CO_2 ABSORBER
LEAN MEA COOLER
EXISTING FURNACE STACK
REBOILER
PUMP
MEA + CO_2
PUMP
DOWTHERM
PUMP
MEA-MEA EXCHANGER
FURNACE FLUE
MEA SOLUTION

Figure 1. Schematic diagram of IGT gas-generating system



2a. Natural gas reforming system

2b. Reformer controls and synthetic gas mixing panel
synthetic gas mixing panel

Figure 2. Gas-generating system

DESCRIPTION OF FURNACE TEST FACILITY

The experimental work was conducted on a rectangular furnace with a 25-sq ft cross-sectional area and a 13-foot length. This furnace can be end- or sidewall-fired at a rate of 4 million Btu/hr. The furnace is equipped for in-the-flame sampling, preheated air, and flue-gas recirculation. (See Figure 3.) This furnace is capable of operating at temperatures of up to 3000°F or as low as 1600°F at a constant (maximum) gas input of 4 million Btu/hr and up to 40% excess air. Cooling is achieved with cooling coils embedded in the refractory walls. The furnace is constructed completely of 9-inch thick cast refractories, with removable panels in one sidewall to permit insertion of sampling probes (Figure 4). The overall furnace system is shown schematically in Figure 5. The system is flexible enough so that the following operating parameters can be independently varied:

- Heat input, up to 4 million Btu/hr (6.0 million for certain burners)
- Air input, up to 40% excess
- Heat losses to the furnace walls by changing flow in water-cooling tubes cast into the refractories
- Combustion air temperature, up to 1000°F
- Flue-gas recirculation capability, up to 15% of combustion air
- Furnace pressure, up to +0.05 inch of water.

The combustion air for the main furnace can be preheated up to a temperature of 1000°F with a separately fired radiant tube air preheater. The radiant tube furnace (Figure 6) consists of an insulated airtight steel chamber 4 feet high, 4 feet wide, and 16 feet long. As the combustion air to be preheated passes through this chamber, it is heated by convection from three 6-inch diameter "hairpin" gas-fired radiant tubes.

The radiant tubes and refractory flow passages inside the preheater are arranged to provide an S-shaped flow pattern, which maximizes residence time for heating at the maximum allowable pressure drop (20 ounces) for which the flow pattern will provide the necessary air flow of 75,000 SCF/hr.

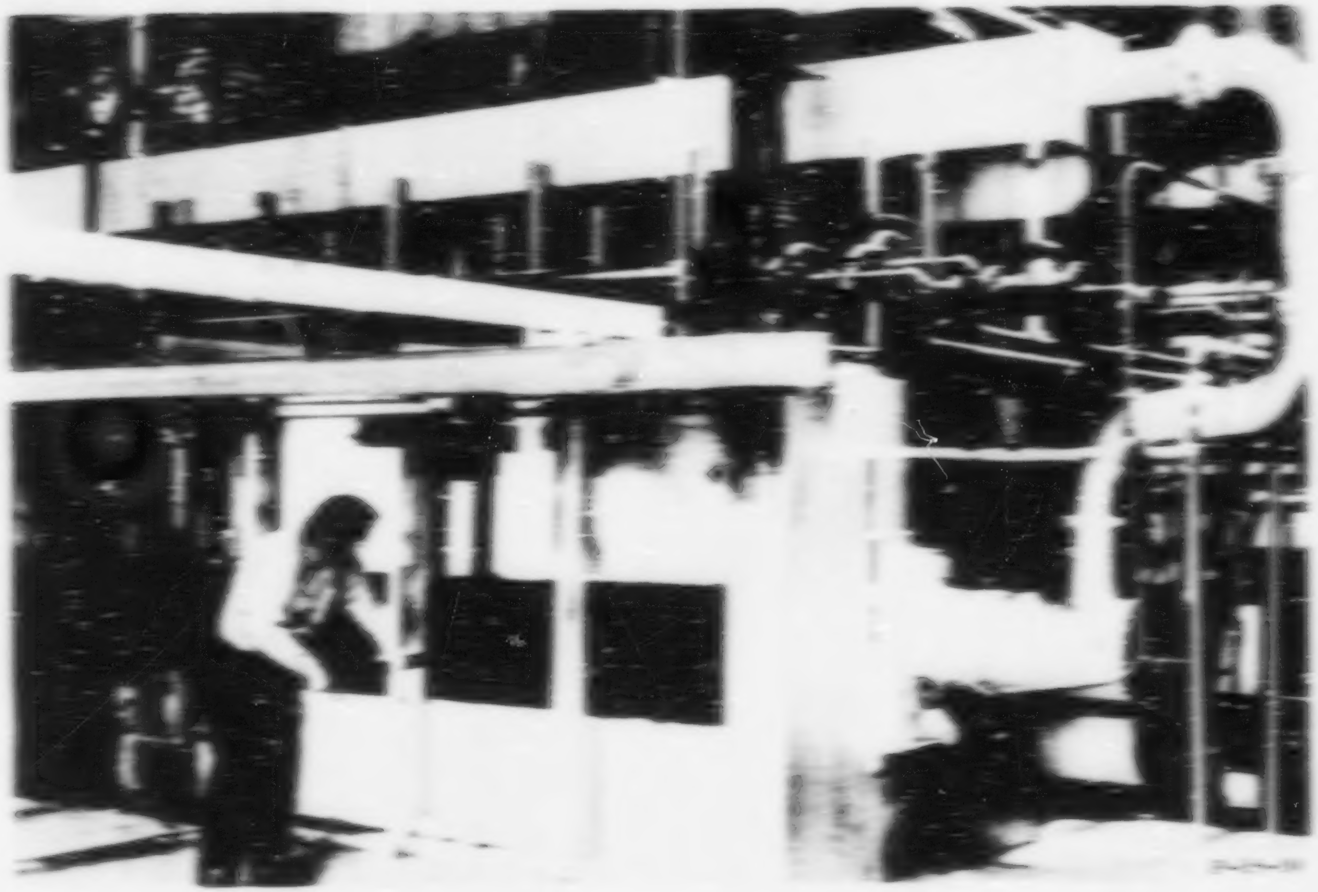


Figure 1. Rectangular test furnace

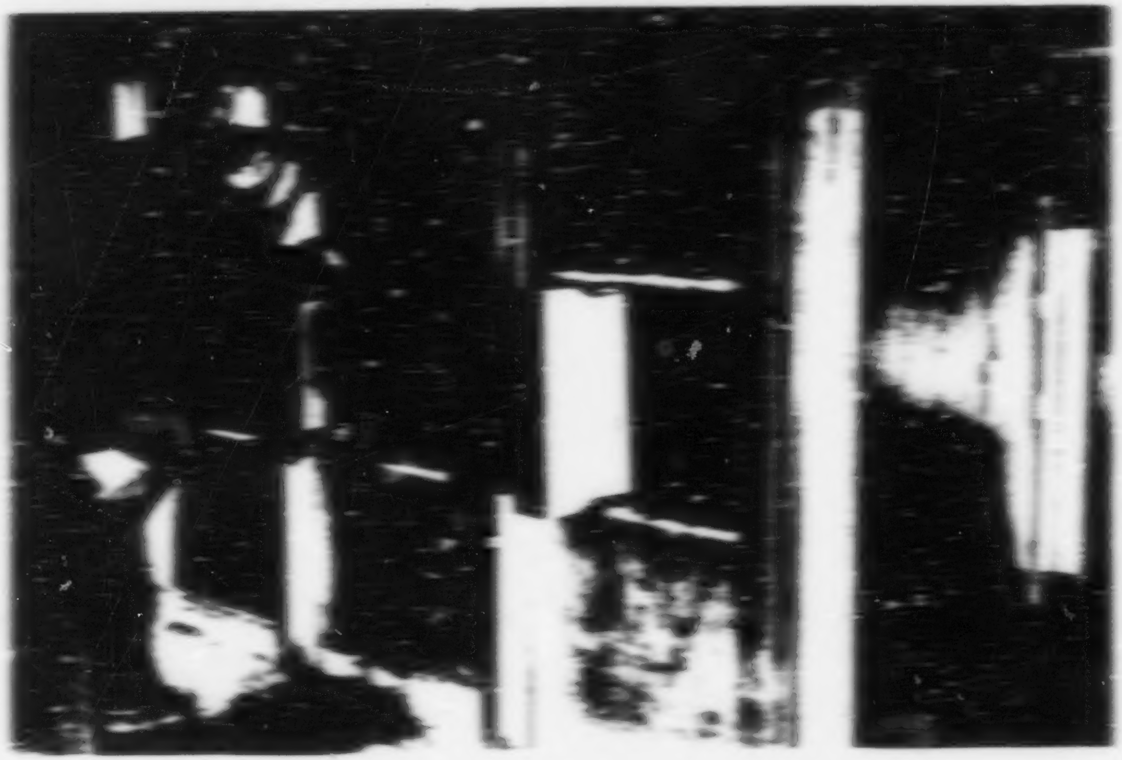


Figure 4. Removable sidewall furnace panels for interior flame probing

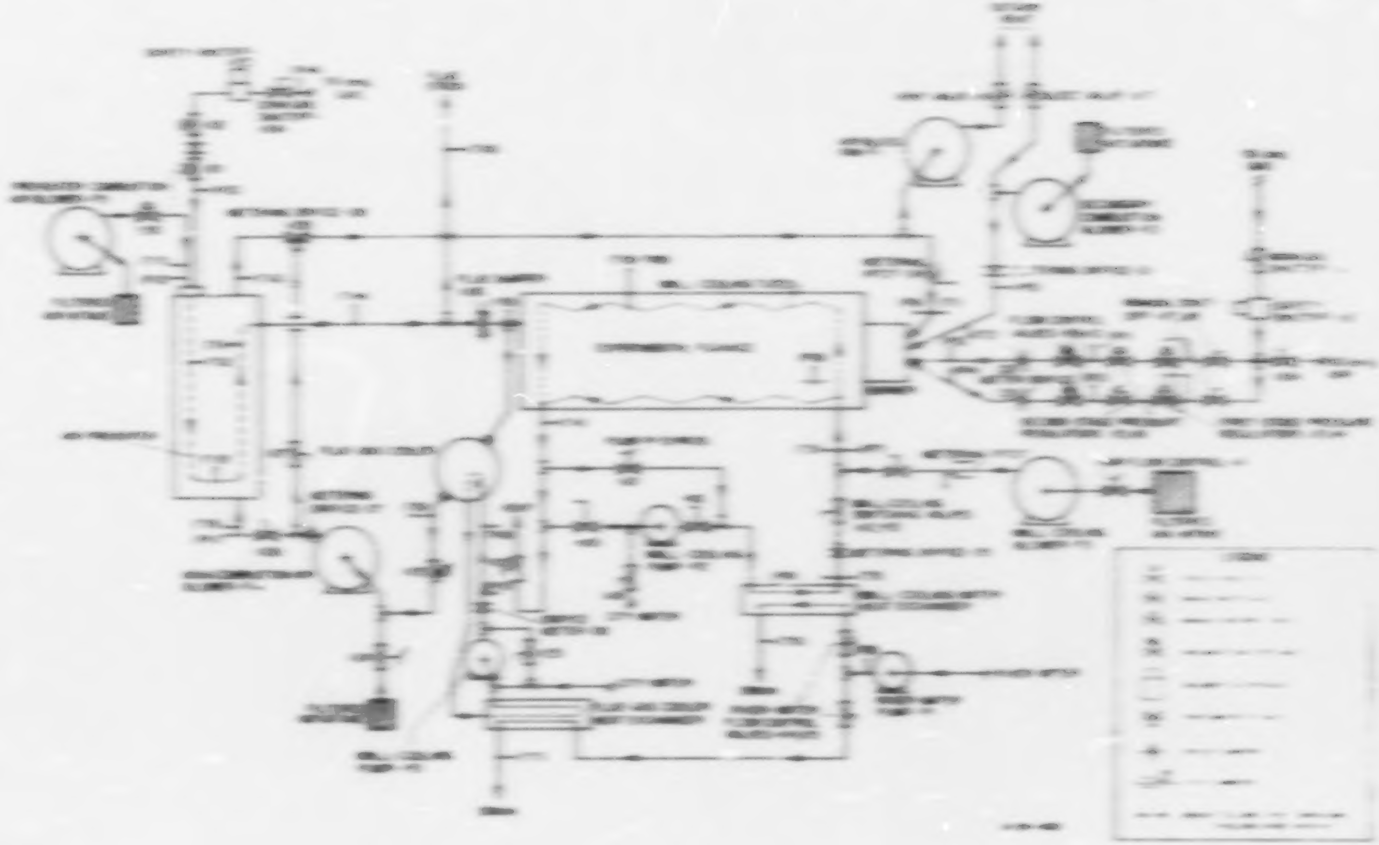


Figure 5. Overall system schematic diagram of rectangular test furnace system

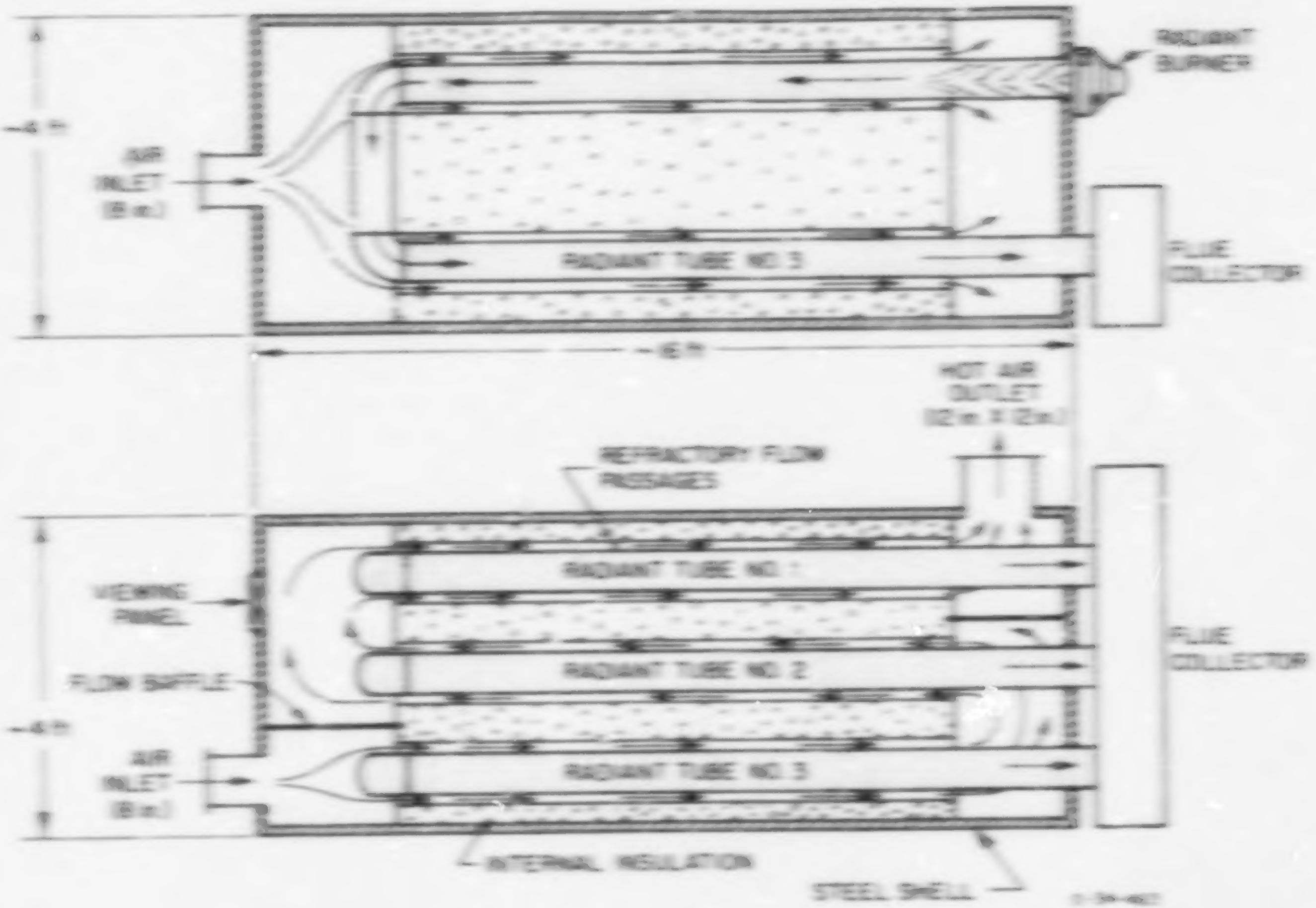

RADIANT BURNER
AIR INLET (8 in.)
~4 ft
RADIANT TUBE NO. 3
FLUE COLLECTOR
~16 ft
HOT AIR OUTLET (12 in. X 12 in.)
REFRACTORY FLOW PASSAGES
VIEWING PANEL
RADIANT TUBE NO. 1
RADIANT TUBE NO. 2
FLOW BAFFLE
~4 ft
AIR INLET (8 in.)
RADIANT TUBE NO. 3
FLUE COLLECTOR
INTERNAL INSULATION
STEEL SHELL

Figure 6. Radiant tube preheater for main furnace combustion air

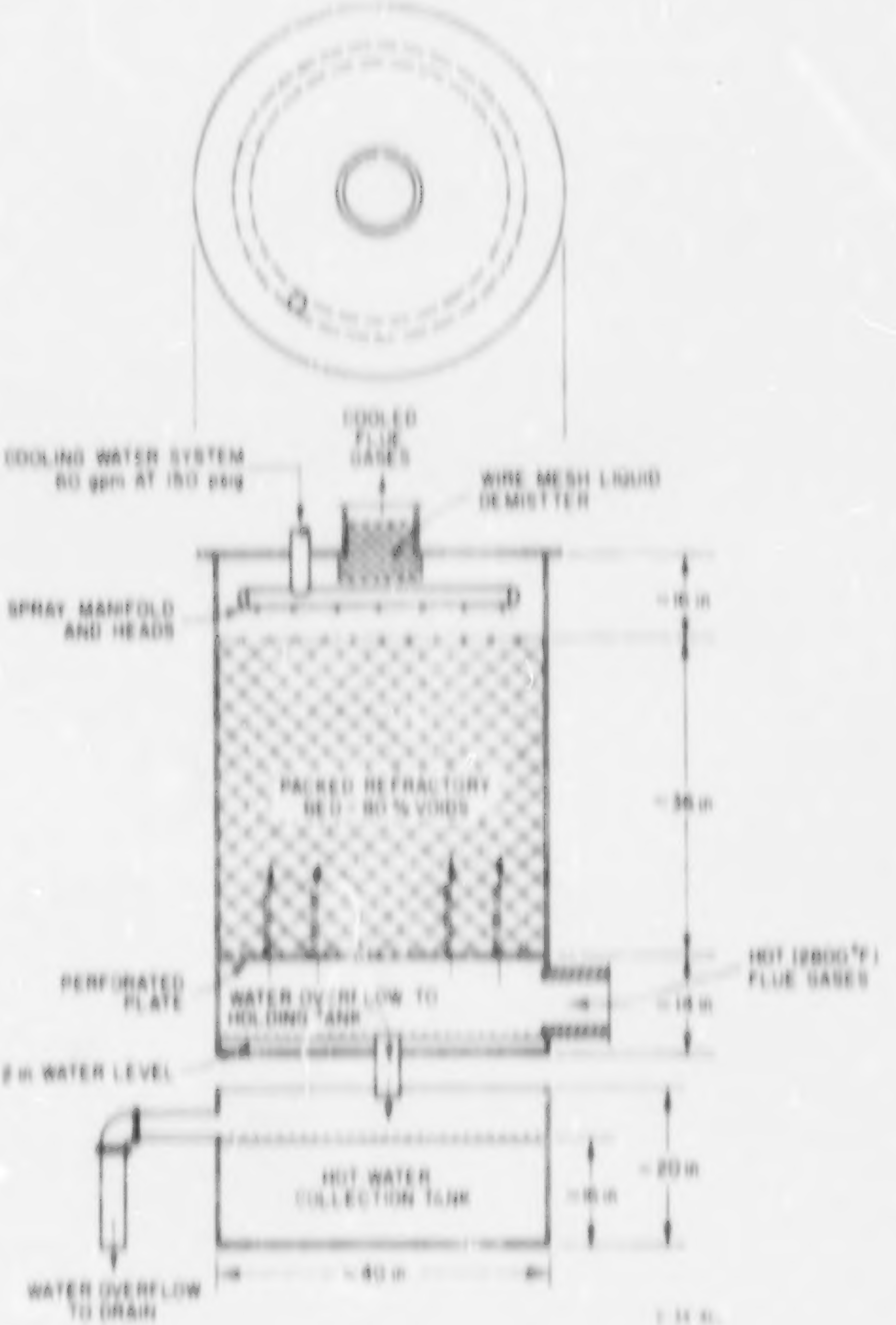

COOLED FLUE GASES
COOLING WATER SYSTEM 60 gpm AT 150 psig
WIRE MESH LIQUID DEMISTTER
SPRAY MANIFOLD AND HEADS
≈ 16 in
PACKED REFRACTORY BED - 80 % VOIDS
≈ 36 in
HOT (2800 °F) FLUE GASES
PERFORATED PLATE
WATER OVERFLOW TO HOLDING TANK
≈ 16 in
2 in WATER LEVEL
HOT WATER COLLECTION TANK
≈ 16 in
≈ 20 in
WATER OVERFLOW TO DRAIN
≈ 40 in

Figure 7. Flue-gas cooler

The temperature of the air can be regulated by changing the heat input to the radiant tubes. Ambient temperature air can be supplied by completely shutting down the preheater or by directing the air through the preheater bypass pipe. The bypass pipe was installed to allow working on the preheater without shutting down the air supply to the main furnace. Air bypass is achieved by selective switching of valves.

Flue products for recirculation back to the burner and main furnace are obtained from the furnace itself. Flue products can be withdrawn from the furnace flue passage just prior to the main furnace flue damper. Up to 14,000 SCF/hr of flue products can be withdrawn from the flue, which provides a 30% recirculation factor when the furnace is fired at 3.5 million Btu/hr with 20% excess air.

The main furnace flue products are actually pulled from the flue (Figure 5) by the suction in the inlet side of the main furnace combustion air fan (F4). The flue products enter the recirculation withdrawal and treatment system at about 2800°F through a short length of internally insulated steel duct. These hot gases are cooled to about 125°F in a packed-bed water cooler (Figure 7). Cooled city water (about 70°F) is sprayed down on a bed of refractory packings as the hot gases pass up through the packed bed. This cooling system lowers the water content of the flue gas from about 0.008 to about 0.007 lb/CF, which is the dew point of the gases at about 125°F. (The lost water content can be added again later in the system if experimental conditions require this treatment.) The cooled gases then pass through a flow-control shutoff valve (V25 in Figure 5). This valve controls the flue-gas flow rate, which regulates the percentage of recirculated products. This valve is interlocked to an outlet temperature sensor on the gas cooler. If the outlet temperature of the gases exceeds 150°F, which would damage the combustion air fan, the control valve (V25) shuts down. This stops the flow of flue gases. Beyond the flue-gas control valve, the flue gases are mixed with the required amount of air for combustion. A control valve (V24) regulates the amount of air pulled in by the fan. The total amount of air for combustion and flue products is metered with an orifice plate (O7) at the outlet of the fan. The flue products and air then pass into the air preheater or preheater bypass pipe.

The water used in the flue-gas cooler is clean city water, which is continuously recycled. A water flow of 60 gpm is supplied at 150 psig by a turbine pump to a series of spray heads in the gas cooler. The hot (200°F) spent water flows out of the cooler into an atmospheric holding tank. This tank is equipped with a constant-level overflow to the building drain. In this way, any condensed water from the combustion is removed and disposed of in the sewer. The water in the holding tank is periodically treated with sodium hydroxide to prevent acid buildup in the water due to condensing flue-gas components. One such component removed by the flue-gas cooler is NO_2. The hot water from the water holding tank is cycled through an American Standard heat exchanger capable of removing 1.5 million Btu/hr of heat from the water. Cooling in the heat exchanger is provided by a flow of river water at a rate of about 150 gpm at 80 psig. The river water is supplied by a river adjacent to the test facility through a service pump (P1 in Figure 5) maintained by IGT.

Figure 8 is an overall view of furnace controls and the analytical instrumentation package. The equipment used for concentration measurements of chemical species during this program is listed below; these analyzers included the following items:

1. Beckman 742 Polarographic Oxygen (O_2)
2. Beckman Paramagnetic Oxygen (O_2)
3. Beckman NDIR Methane (CH_4)
4. Beckman NDIR Carbon Monoxide (CO)
5. Beckman NDIR Carbon Dioxide (CO_2)
6. Varian 1200 Flame Ionization Chromatograph (Total HC and C_2 to C_9)
7. Beckman NDIR Nitric Oxide (NO)
8. Beckman UV-NO_2
9. Hewlett-Packard Thermoconductivity Chromatography, Hydrogen (H), Nitrogen (N_2), Argon (A_2), CO, CO_2, C_1 to C_5, Oxygen (O_2)
10. Beckman Chemiluminescent NO-NO_2
11. Data Integration System.

This instrumentation package allowed concentration measurements of the following major components: 1) measurement of hydrocarbon compounds C_1 to C_9;

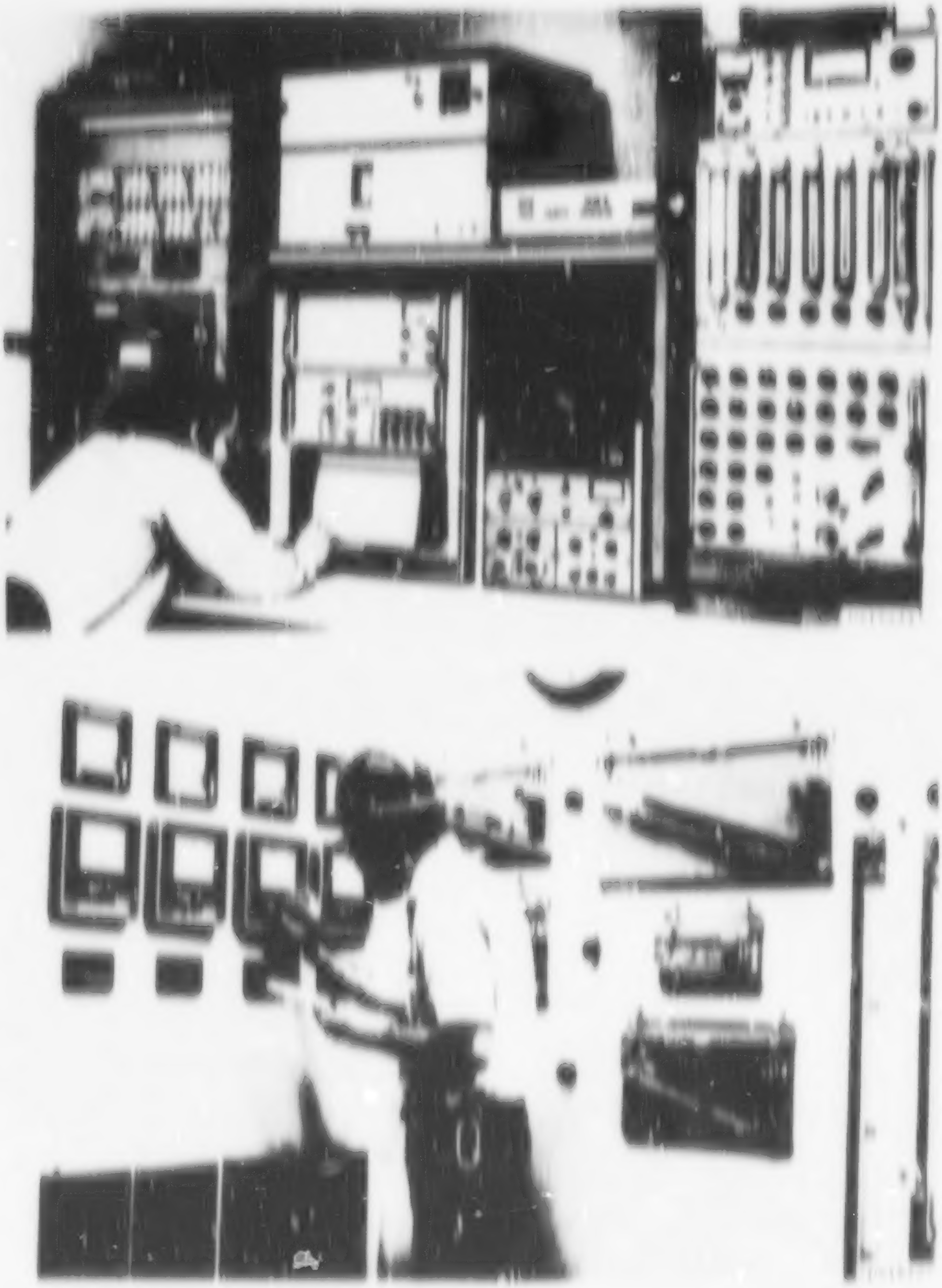


Figure 8. Control room facility and analytical instrumentation

2) independent check of NO-NO_2 chemiluminescent with NDIR-NO and NDUV-NO_2; 3) independent check of paramagnetic O_2, polarographic O_2, NDIR-CH_4, NDIR-CO, and NDIR-CO_2 with the respective chromatographic species concentration; and 4) measurement of hydrogen (H_2), argon (A_2), and nitrogen (N_2).

The following sections give a general description of the measurement system used for this program.

NO AND NO_2 INSTRUMENTATION

The chemiluminescent NO_x and NDUV-NO_2 system was mounted in a roll-around cabinet that could be placed out at the furnace. This was important in minimizing sampling distances, which can affect accuracy. The chemiluminescent unit was equipped with a carbon converter. Test work by IGT and others has demonstrated that in a reducing environment the carbon converter maintains a better conversion efficiency than converters made of stainless steel, quartz, or molybdenum.

The instrumentation was calibrated by using both a permeation tube with a controlled known release of NO_x and certified prepared cylinders of NO and NO_2 gases.

The sample gas was drawn from the furnace through a special alumina probe by a Dia-Pump Model 08-800-73 all stainless-steel and Teflon® pump delivering approximately 0.4 CF/min. (This sample delivery rate was dictated by the requirements of the measuring instruments.) The sample is immediately passed through a stainless-steel large-particle filter. Both the pump and filter were kept above 100°C to prevent condensation of the water vapor inherent to combustion products.

CO, CH_4, AND CO_2 MEASUREMENTS

Nondispersive infrared analyzers were used for carbon monoxide, methane, and carbon dioxide measurements. These analyzers do not affect the sample gas and can be operated in series. They were calibrated by using certified gases with known concentrations of the species being determined. The infrared analyzers require a completely dry sample. Therefore, the sample was first passed through a water trap and a 3 Å molecular drying sieve. A small in-line filter was placed immediately after the drying tube to trap particles of sieve that may be carried over by the gas stream.

OXYGEN MEASUREMENTS

A portion of the "conditioned" sample gas is diverted from the NDIR units to a Beckman Model 600 paramagnetic analyzer. A second oxygen analyzer, a Beckman Model 742 polarographic, was used as a cross-check on the oxygen concentration. The Model 742 analyzer has an advantage over the paramagnetic in time response.

CHROMATOGRAPHIC MEASUREMENTS

Because a detailed gas analysis was required, the sample was fed to a Hewlett-Packard 7620-A thermal conductivity chromatograph, which permitted concentration evaluations of hydrogen, nitrogen, argon, oxygen, carbon monoxide, carbon dioxide, and hydrocarbons C_1 to C_5. To achieve separation of these species, a helium carrier gas was used in conjunction with a Porapak Q column. Three temperature program rates were also required, ranging from -100° to 300°C. A sample loop volume of 100 ml was used to ensure linearity in the hydrogen response for concentrations up to 60%.

For total hydrocarbon analysis, a Beckman hydrocarbon analyzer was used. A detailed hydrocarbon analysis could be made using a Varian 1200 flame-ionization chromatograph. All chromatographic readings were electronically integrated and printed out as a function of resolution time.

In addition to flue-gas analysis, a major task of this program was to map profiles of temperature, chemical species, and flame emissivity. Modified designs of the International Flame Research Foundation (IFRF) were used to construct probes, which enabled this type of data collection.

Figure 9 shows the assembly drawing of the gas-sampling probe used in both the flame and the flue. To minimize NO_2 reduction in the probe, an alumina tube was inserted for the first 18 inches and was joined to Teflon tubing to carry the gas sample to the analyzers.

Temperature data were collected using a suction pyrometer; the design is illustrated in Figure 10. A Pt-Pt Rh 10% thermocouple was used. The efficiency of the pyrometer was measured at 96% with a 25-second response time.

The gas-sampling probe, suction pyrometer, and radiation cooling target were all designed to be installed in the general probe holder shown in Figure 11.

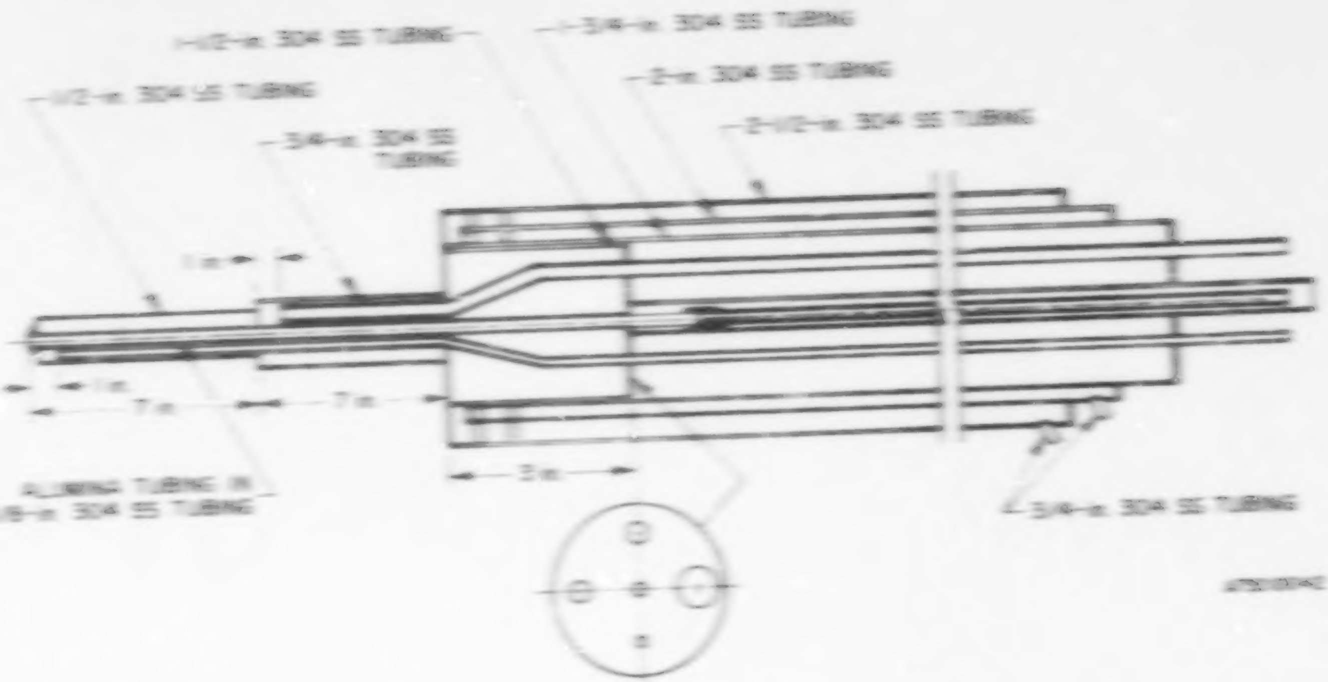

1-1/2-in. 304 SS TUBING
1-3/4-in. 304 SS TUBING
1/2-in. 304 SS TUBING
2-in. 304 SS TUBING
3/4-in. 304 SS TUBING
2-1/2-in. 304 SS TUBING
1 in.
1 in.
7 in.
7 in.
3 in.
ALUMINA TUBING IN
1/8-in. 304 SS TUBING
3/4-in. 304 SS TUBING

Figure 5. Gas-sampling probe head for nonparticulate flue gases

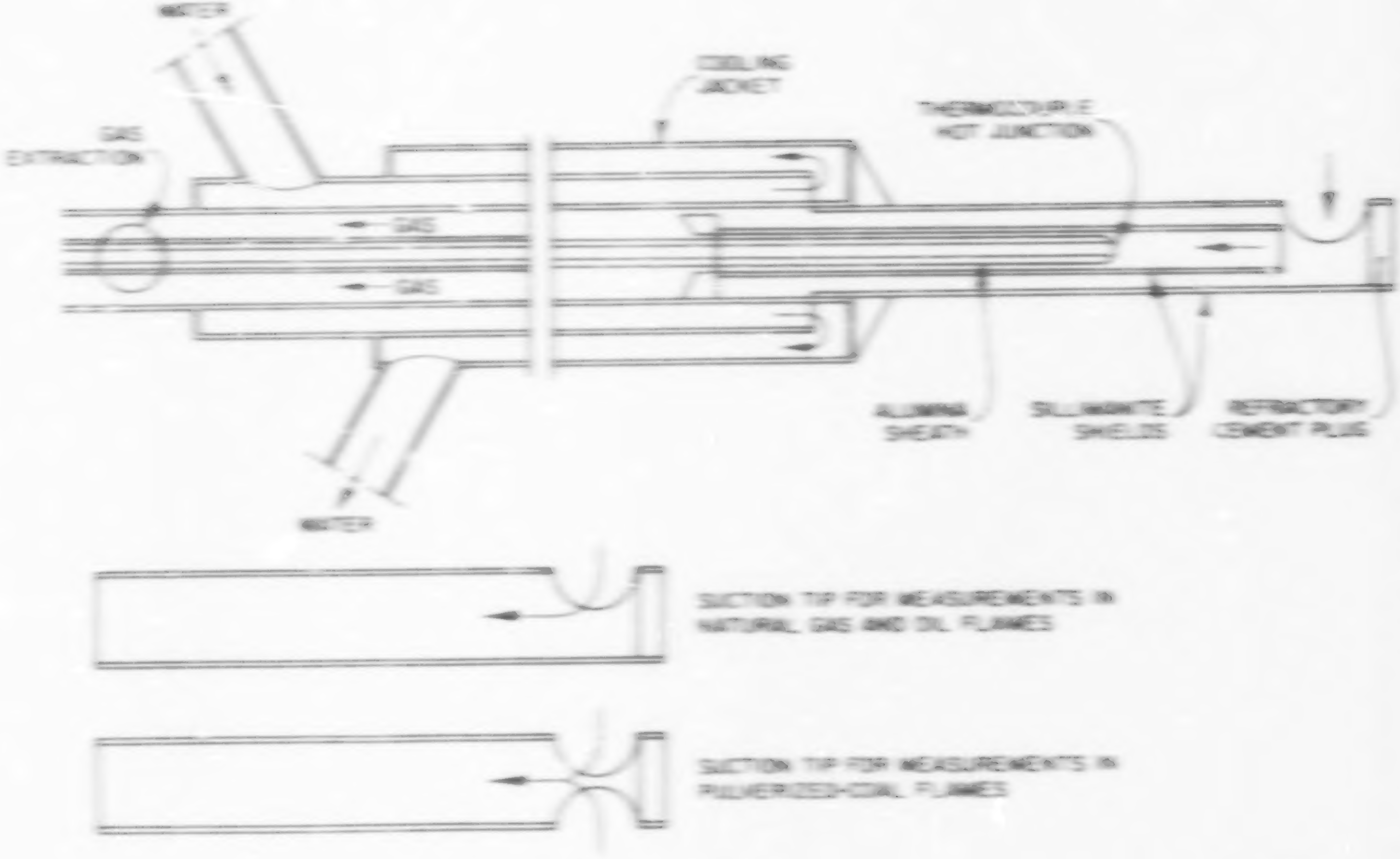

WATER
GAS EXTRACTION
GAS
GAS
COOLING JACKET
THERMOCOUPLE HOT JUNCTION
ALUMINA SHEATH
SILLIMANITE SHIELDS
REFRACTORY CEMENT PLUG
WATER
SUCTION TIP FOR MEASUREMENTS IN NATURAL GAS AND OIL FLAMES
SUCTION TIP FOR MEASUREMENTS IN PULVERIZED-COAL FLAMES

Figure 31. Modified IFRF temperature probe

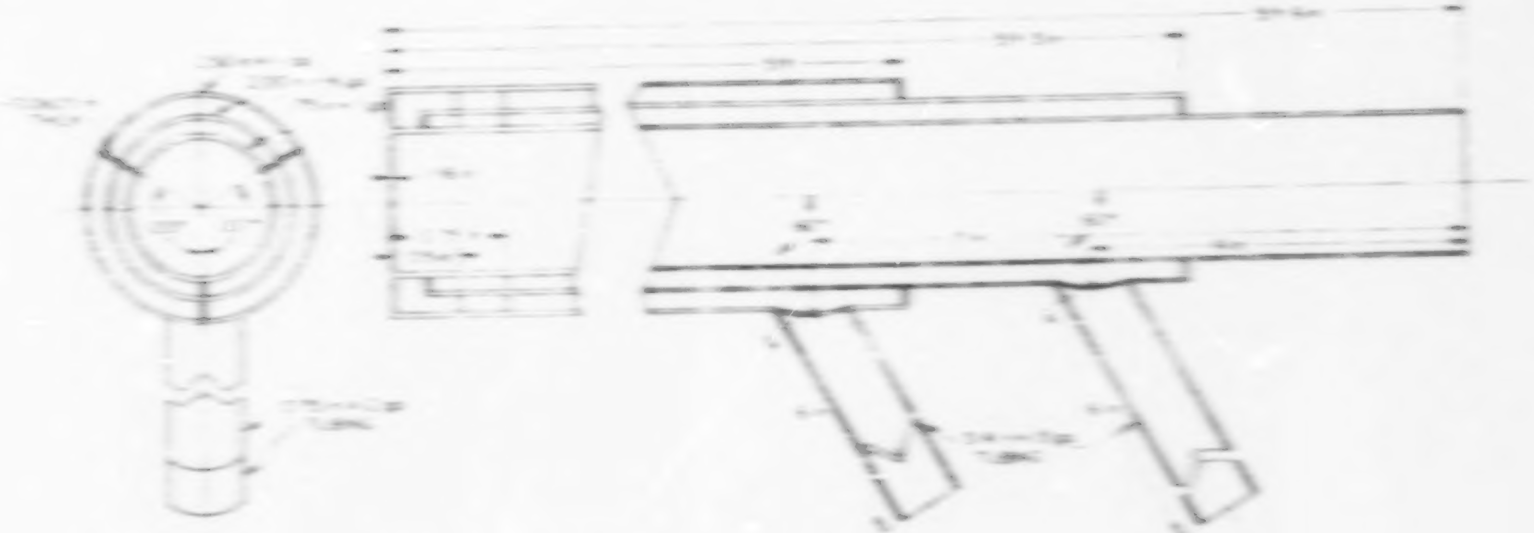


Figure 11. General probe holder

To evaluate radiation intensity, which is needed for a determination of flame emissivity, a PR 200 Pyroelectric Radiometer, manufactured by Molectron Corp. in Sunnyvale, California, was used. Figure 12 shows the pyroelectric radiometer plus radiation shield. This radiometer uses a permanently poled lithium tantalate detector that is capable of resolving radiant power into the nanowatt range while maintaining a continuous spectral response from the vacuum UV to 500μ m. A built-in optical calibration system in the form of a highly stable LED (light-emitting diode) that is calibrated against an NBS traceable standard of total irradiance permits a direct correlation of experimental data from different trials.

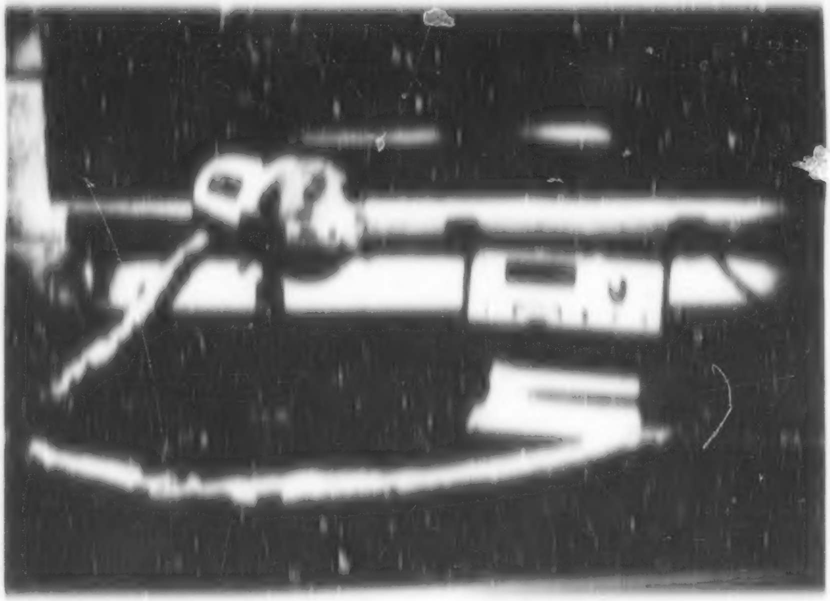


Figure 12. Pyroelectric radiometer
(used for emissivity measurements)

EXPERIMENTAL PLAN

All test data were collected using a single-register movable-vane boiler burner with an axial fuel injector. An assembly drawing of the MVBB tested is shown in Figure 13. The combustion air enters perpendicular to the axis of the burner and passes through a register of guide vanes that impart a degree of spin to the air, dependent on the vane orientation. Figure 14 illustrates how the angle of the movable vane is measured. The ratio of the average tangential and radial velocity components at the exit of the movable-vane register depends only on the geometric dimensions of the vanes in the axis perpendicular cross section (assuming a negligible Reynolds number influence).

A straight pipe was used as the fuel injector, guaranteeing that the fuel had only an axial velocity. This type of injector was used for two reasons. First, this type of nozzle would be the most stringent test for flame stability in the cold-wall stability tests; and, second, medium- and low-Btu gases would normally be available at relatively low pressures, dictating the use of a low-pressure injector. The diameter of the fuel injector was varied for fuel type to maintain an injection velocity of 100 ft/s.

The burner block used during this program had a 30-degree divergent angle with a 15.2-cm (diameter) entrance and a 48.2-cm (diameter) exit to the furnace. To maximize flame stability the throat nozzle position was used throughout this program. The throat nozzle position is located 4.5 cm from the burner block entrance within the 15.2-cm (diameter) refractory duct connecting the burner with the block.

Burner operating conditions used throughout the program had the level of flue oxygen fixed at 3% with the combustion air preheated to 325°F (unless specified differently). These conditions are considered typical for utility boiler burners.

Based on the overall program objective of evaluating boiler performance changes when retrofitting from natural gas to medium- and/or low-Btu gas, it was necessary to select an operating variable to model the pilot-scale test furnace against a field service boiler. Several parameters were considered, including operating wall temperature, heat absorption profile, and firing density. It was decided to match the temperature of the combustion products from natural gas at the pilot-scale

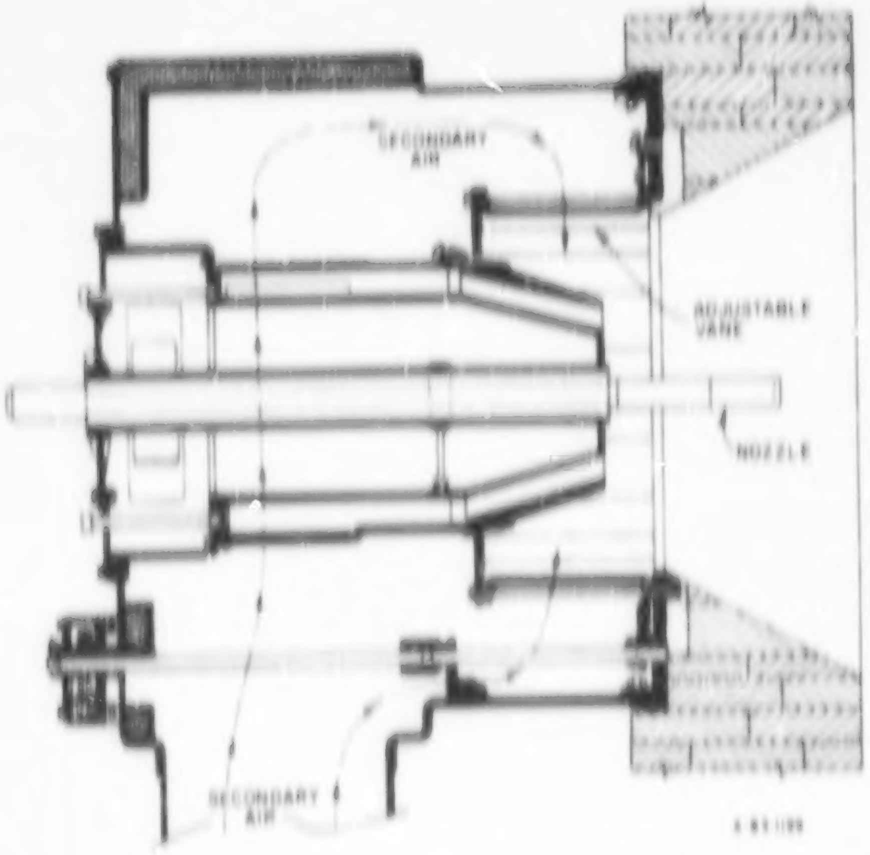

SECONDARY
AIR
ADJUSTABLE
VANE
NOZZLE
SECONDARY
AIR

Figure 13. Diagram of movable-vane boiler burner

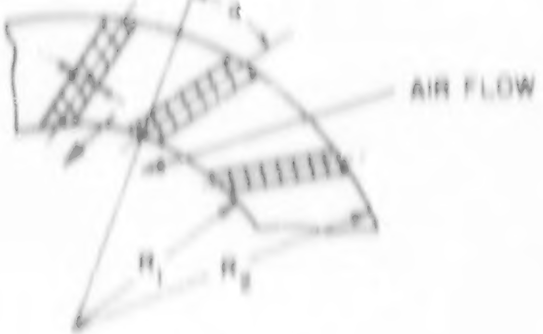

α
AIR FLOW
R_1
R_2
A-34-414

Figure 14. Method of measuring movable-vane angle for boiler burner

furnace exit to the temperature measured between the boiler and the secondary superheater section of a utility boiler. This decision was based on the complexities of multiburner interactions within a utility boiler versus the single-burner test furnace, where several flames would not view the boiler water walls. The data of most interest in evaluating performance changes were gas volume, temperature, and gas emissivity entering the secondary superheater. Thus, baseline data were collected for natural gas after the furnace load had been adjusted to give an exit-gas temperature of 2550°F.

The first task to be conducted after the baseline furnace operating conditions had been fixed was to determine flame stability. The stability trials were to be conducted under the most stringent operating conditions, that is, with the furnace walls, burner block, and combustion air at ambient temperature.

The second problem addressed was the relative flame length of the medium- and low-Btu gases compared with natural gas. It was anticipated that flame length changes could affect the rate of heat transfer from the flame to the boiler tubes through a change in flame emissivity. If the flame length change resulted in a lower heat removal within the boiler, the combustion products entering the secondary superheater would be at a higher than normal temperature. This condition could result in tube damage or a loss in efficiency, because the convective section would be undersized. Using the burner and furnace operating conditions outlined for the baseline tests, flame length measurements were made as a function of vane angle for each test gas. In each case, measurements were taken only after the exit-gas and furnace-wall temperatures had stabilized. As stated above, a straight nozzle was used with a diameter giving a fuel velocity of 100 ft/s. The criterion for evaluating the end of the flame was when 1% of the total gas-sample volume was combustible.

The third problem to be answered by this program was what would be the changes in efficiency — that is, the fraction of total enthalpy input transferred to the load — when retrofitting a unit designed for natural gas with a medium- or low-Btu gas. Detailed temperature and emissivity data were collected for each test gas. These measurements provide not only the information needed to evaluate changes in efficiency within the boiler but also the data that can be used by manufacturers to calculate any redesign that may be needed in the convective passes.

The final question addressed by the program was the level of NO emissions from each test fuel gas and how it compares with emissions from natural gas combustion. These data are presented in detail and analyzed in the "RESULTS" section.

RESULTS

During the flame stability trials, fuel-gas velocities from 25 ft/s up to 500 ft/s were investigated. The optimum fuel-gas injection velocity range was 75 to 200 ft/s. Above 200 ft/s the flame began to lift (detach) from the injector, and below 75 ft/s the flame became lazy and buoyed badly (moved toward the furnace roof). A velocity of 100 ft/s was selected for use throughout the program because the velocity could be maintained for the spectrum of fuel gases being studied using standard pipe sizes.

Figures 15 through 20 show photographs of the flame for each test gas.

FLAME LENGTHS

Table 4 presents the flame length data determined by radial scans at various points down the furnace axis. The end of the flame was defined as the point where 99% of the fuel was consumed. In general, the flame length decreased with increasing burner vane angle, except for the 60-degree angle natural gas and Wellman-Galusha air, which exhibited longer flames than the corresponding 45-degree burner vane angle. All medium- and low-Btu fuel-gas flames tested were shorter than the natural gas flames except Winkler air at a 45-degree vane angle, which was 21 cm longer than the natural gas flame produced with a 45-degree vane angle.

NITRIC OXIDE EMISSIONS

To determine the environmental impact of retrofitting utility boilers with medium- and low-Btu gases, NO emissions levels were measured as a function of secondary air-preheat temperature for each of the test fuel gases. Baseline NO emission data were collected using natural gas. The combustion-air temperature was varied from ambient to 800°F. Graphs of the experimental results are presented in Figure 21. For the vane orientations studied, the measured NO levels remained relatively constant up to 400°F, above which dramatic increases occurred for the 45-degree and 60-degree angles.

Figure 22 presents NO versus secondary air-preheat temperature test results using Lurgi oxygen gas. The flue concentrations of NO are approximately 50% less than

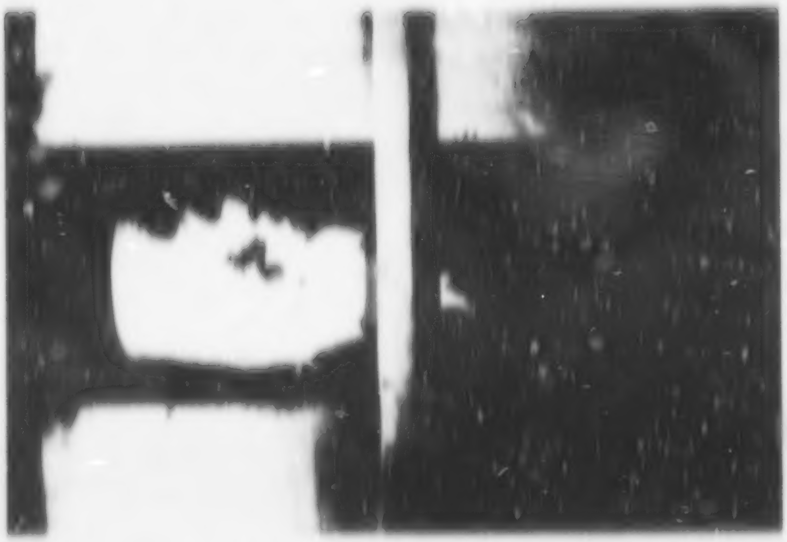


Figure 15. Natural gas flame using a 0.5-inch axial nozzle

Figure 16. Lurgi oxygen gas flame using a 2-inch axial nozzle

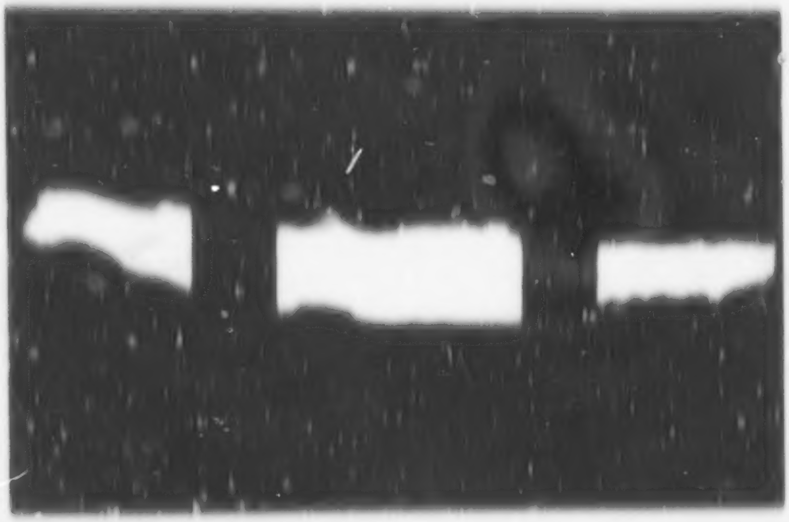


Figure 17. Winkler oxygen gas flame using a 2-inch axial nozzle

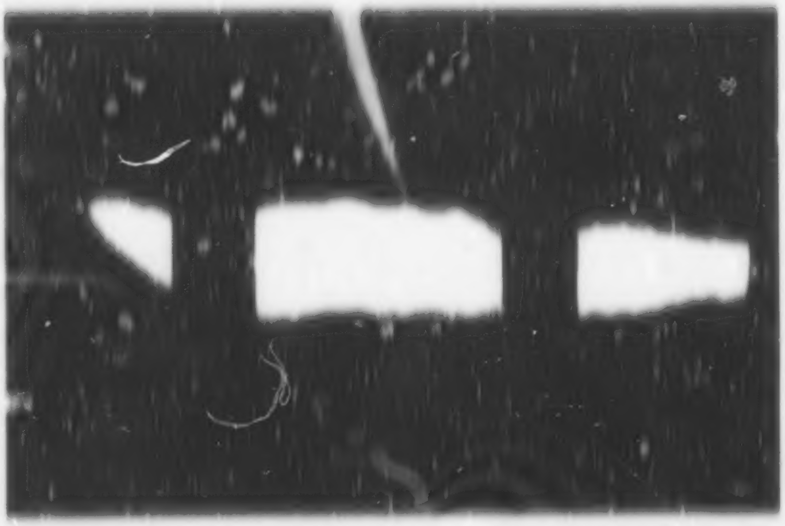


Figure 18. Koppers-Totzek oxygen gas flame using a 2-inch axial nozzle

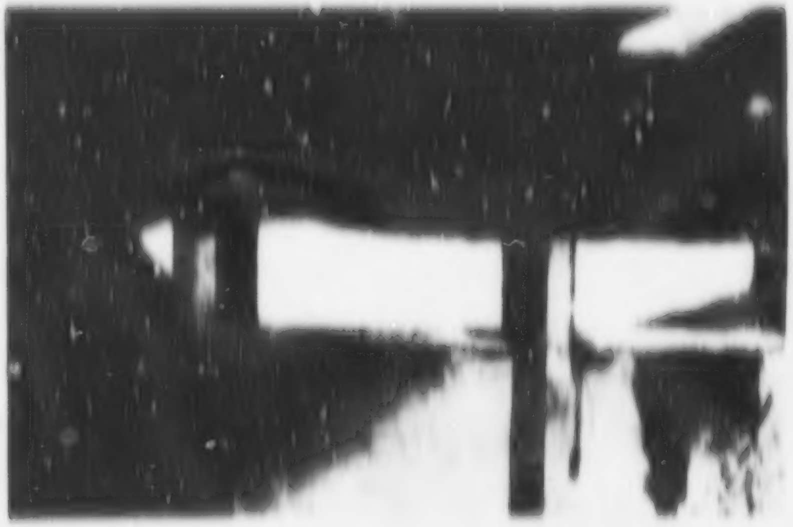


Figure 19. Wellman-Galusha air gas flame using a 1-inch axial nozzle

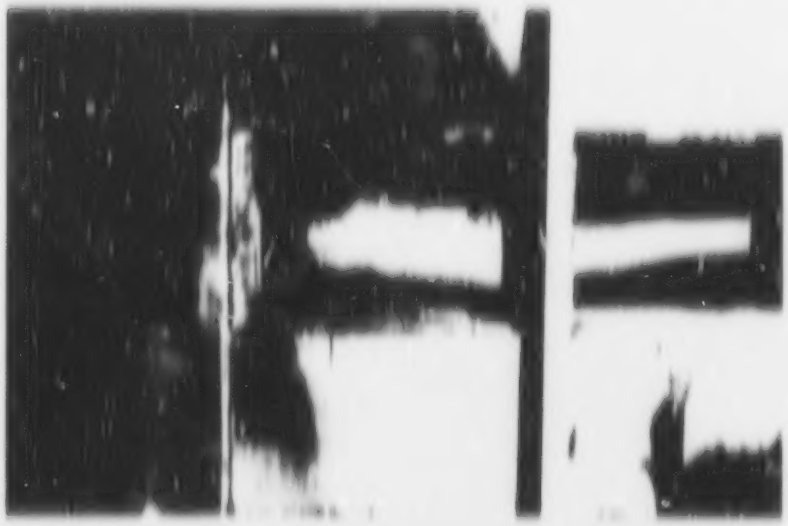


Figure 20. Winkler air gas flame using a 1-inch axial nozzle

Table 4. FLAME LENGTH (cm) AS A FUNCTION OF FUEL TYPE AND VANE ROTATION

Fuel	Vane angle			
	15°	30°	45°	60°
Natural gas	290	250	219	226
Lurgi oxygen	250	227	208	157
Winkler oxygen	250	208	188	146
Koppers-Totzek oxygen	281	208	188	156
Wellman-Galusha air	250	226	108	198
Winkler air	250	250	240	208

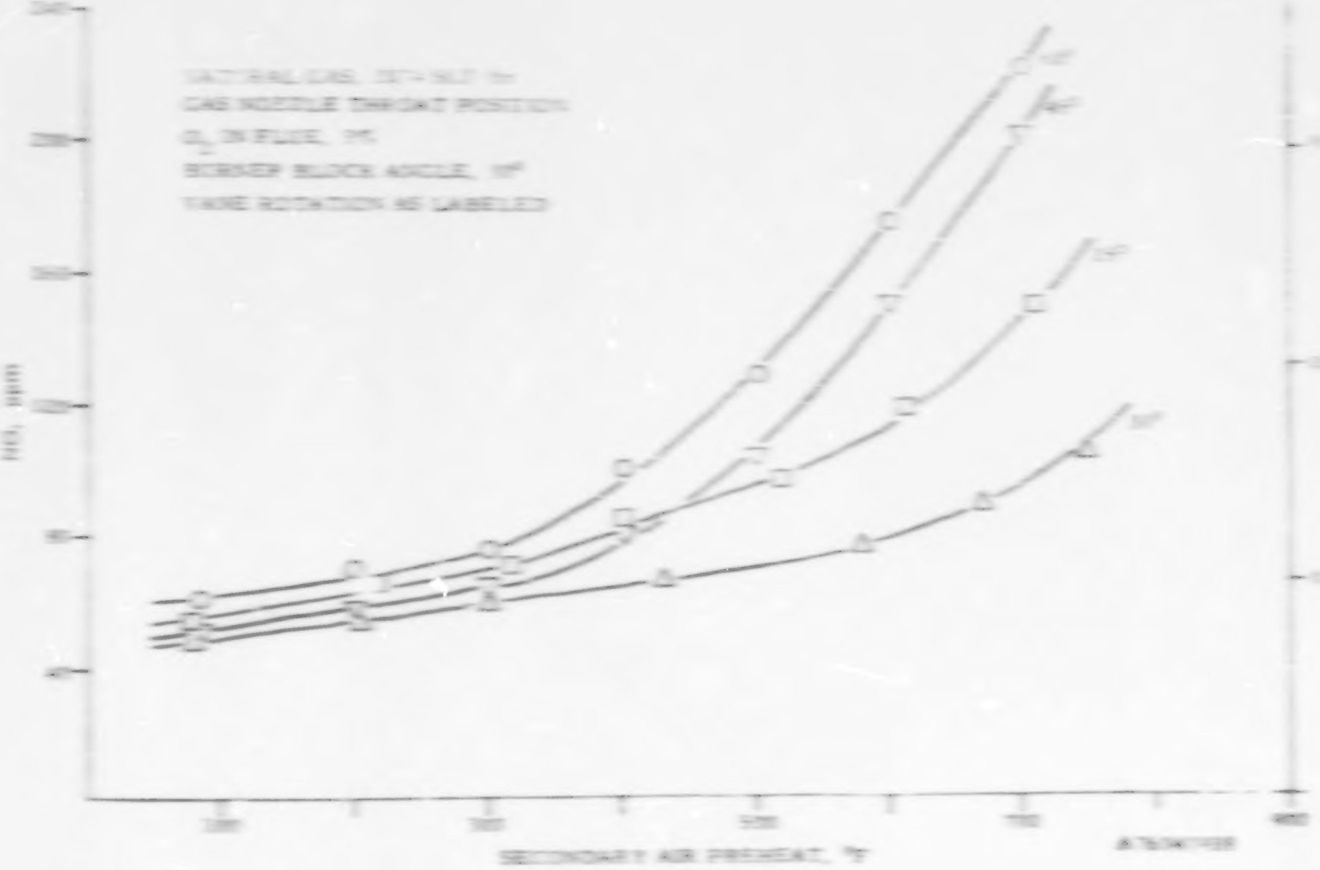


Figure 21. NO versus secondary air preheat with natural gas

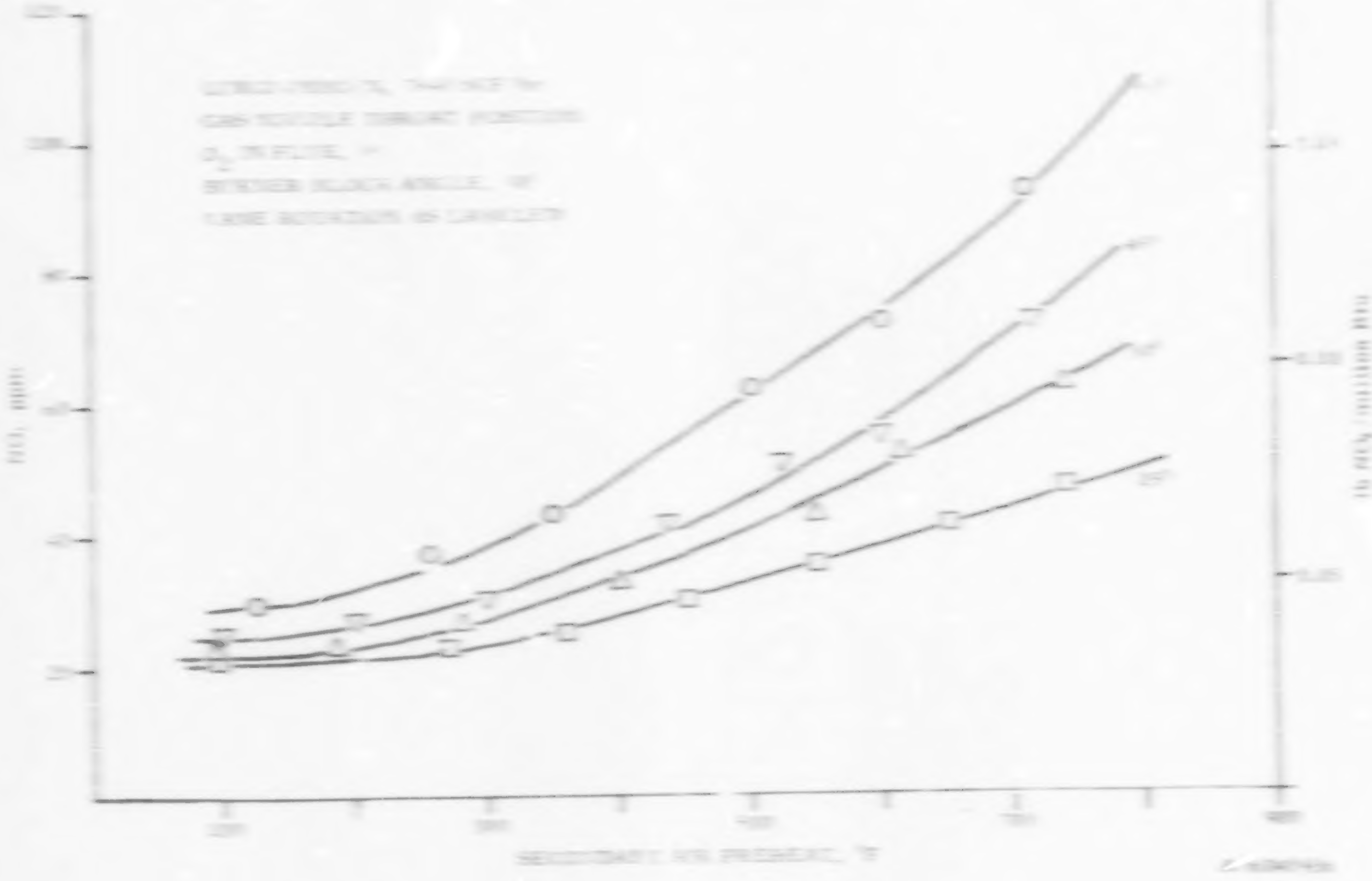


Figure 32. NO versus secondary air preheat with Lurgi oxygen gas

with natural gas for all test conditions. For the detailed burner operating conditions (15-degree vane angle, 125°F air-preheat temperature), the NO level was reduced from 65 ppm (natural gas) to 32 ppm (Lurgi oxygen gas). These emission reductions were expected based on an adiabatic flame temperature comparison, because Lurgi oxygen has a 173°F lower temperature than natural gas.

Flue levels of NO measured as a function of combustion-air temperature with Koppers-Totzek oxygen gas are shown in Figure 23. For all conditions tested, the Koppers-Totzek gas resulted in higher NO emission levels than did natural gas. Again, by comparing the adiabatic flame temperatures listed in Table 3, this result was anticipated because Koppers-Totzek gas has a 241°F higher adiabatic flame temperature than natural gas. For the 45-degree vane angle with a 125°F secondary air-preheat temperature, this is translated into a 60% increase in the NO emission level.

Comparing the adiabatic flame temperatures of Winkler oxygen gas with natural gas shows that the former is 9°F lower. Thus, based only on adiabatic flame temperature considerations, the NO emission levels should be comparable. The NO test results with Winkler oxygen gas are presented in Figure 24. These measured levels were lower than those measured for natural gas, except for the 60-degree vane rotation with secondary air-preheat temperatures below 560°F and the 45-degree vane rotation with preheat temperatures below 400°F. These results indicate that NO formation strongly depends on combustion aerodynamics because the peak flame temperature and the time that the gas is subjected to this temperature are controlled by aerodynamic turbulence. Although average temperatures may be the same in two cases, the NO_x formation can be different if the turbulent temperature fluctuations are different. The temperature dependence of the chemical reaction rate constant can be expressed by the Arrhenius rate law:

$$k(T) = k_0 \exp\left[-E/RT(t)\right] \qquad (1)$$

The time-averaged value would be:

$$\overline{k(T)} = \frac{k_0}{\tau} \int_{t_0}^{(t_0 + \tau)} \exp\left[-E/RT(t)\right] dt \qquad (2)$$

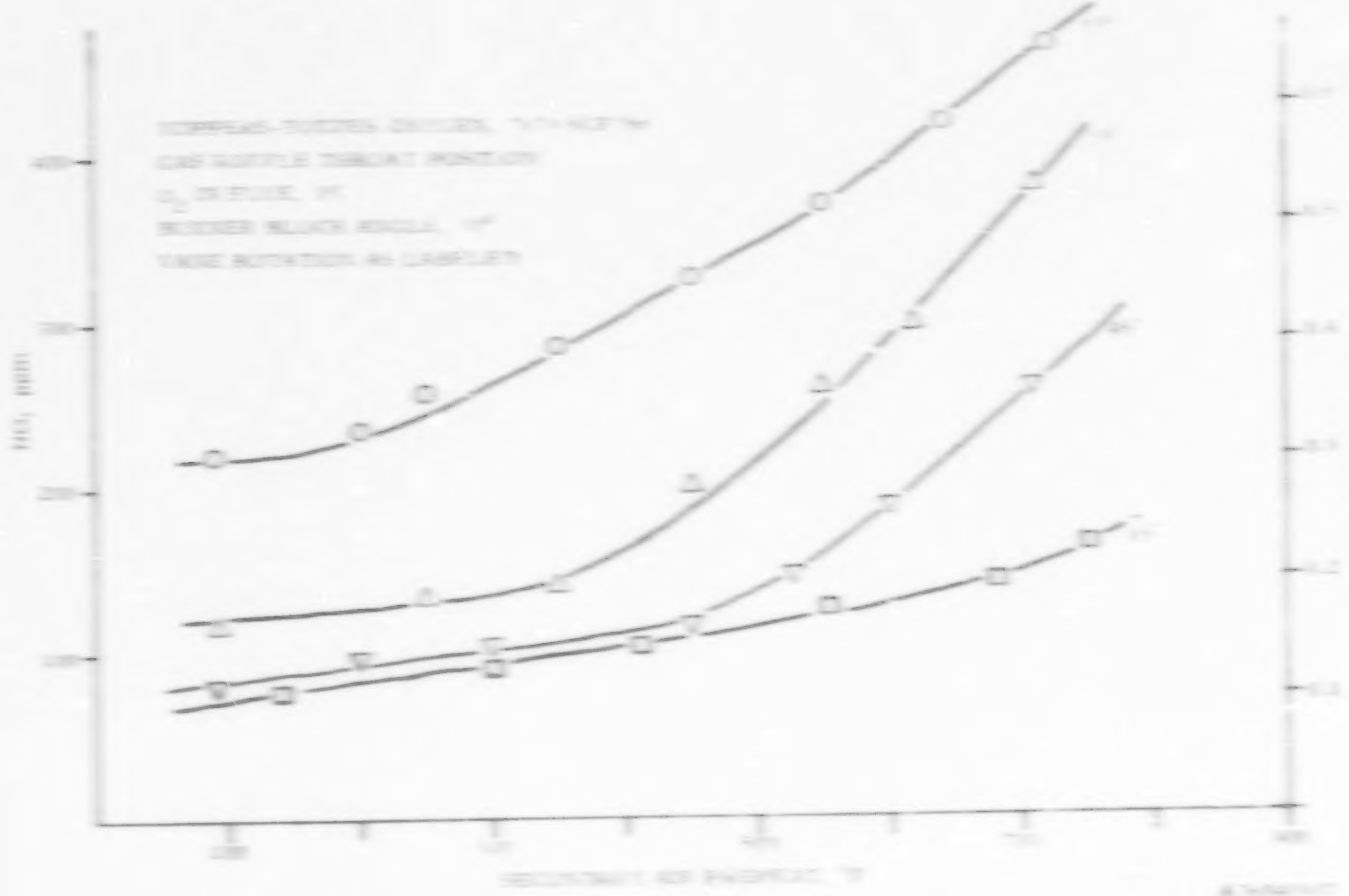


Figure 28. NO versus secondary air preheat with Koppers-Totzek oxygen gas

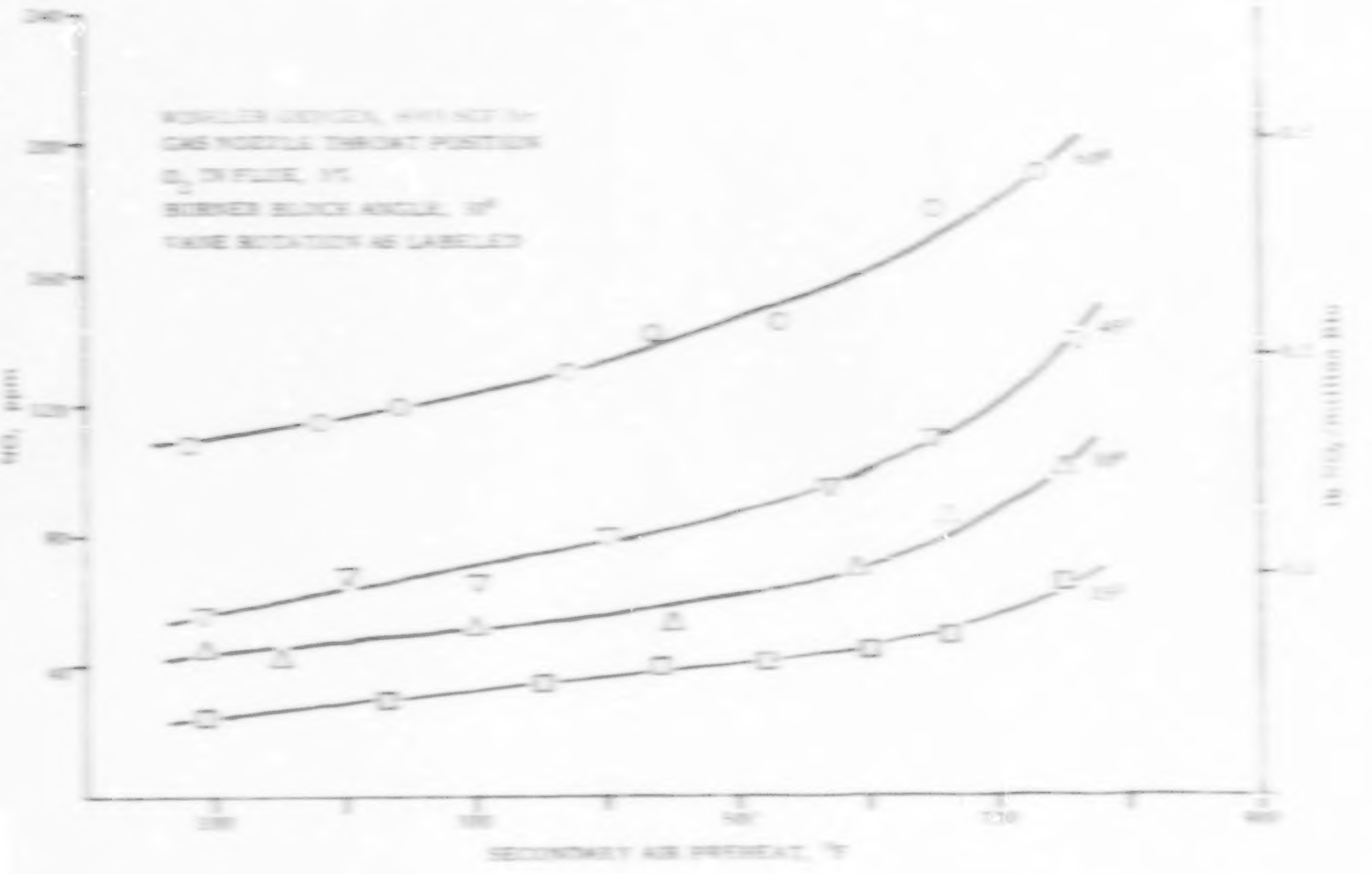


Figure 24. NO versus secondary air preheat with Winkler oxygen gas

for an interval of time, τ , while the rate constant given by the time-averaged temperature would be:

$$k(\overline{T}) = \frac{k_0}{\tau} \exp\left[-E/R\overline{T}\right]. \tag{3}$$

The ratio =

$$K = \frac{\overline{k(T)}}{k(\overline{T})} \tag{4}$$

is always greater than 1 because the exponential nature of the temperature dependence means that the rate constant increase for an increase in temperature above the average exceeds considerably the decrease for a similar reduction in temperature. The value of the ratio, K, depends on the extent and the nature of the temperature fluctuations. Thus, observing that the average temperature (the temperature given by a suction pyrometer) is similar in two cases does not necessarily mean that the NO_x emissions will be similar if the turbulent fluctuations are different. Unfortunately, the technology is not sufficiently advanced to allow measurement of the extreme turbulent temperature pulsations. An additional indication of combustion aerodynamic differences is the reordering of the NO concentration levels as a function of vane angle, which can be seen by comparing Figure 23 with Figure 24.

Figure 25 shows the NO emission data collected for Wellman-Galusha air. The flue concentrations of NO are about 70% lower than those measured for natural gas at the lower air-preheat temperatures. They show an almost linear rise with air temperature. The lack of a dramatic increase in emissions with temperature results in up to a 90% lower NO concentration at elevated combustion-air temperatures for Wellman-Galusha air than for natural gas. Some reduction of NO emissions could be anticipated because of the lower adiabatic flame temperature (2948° versus 3337°F).

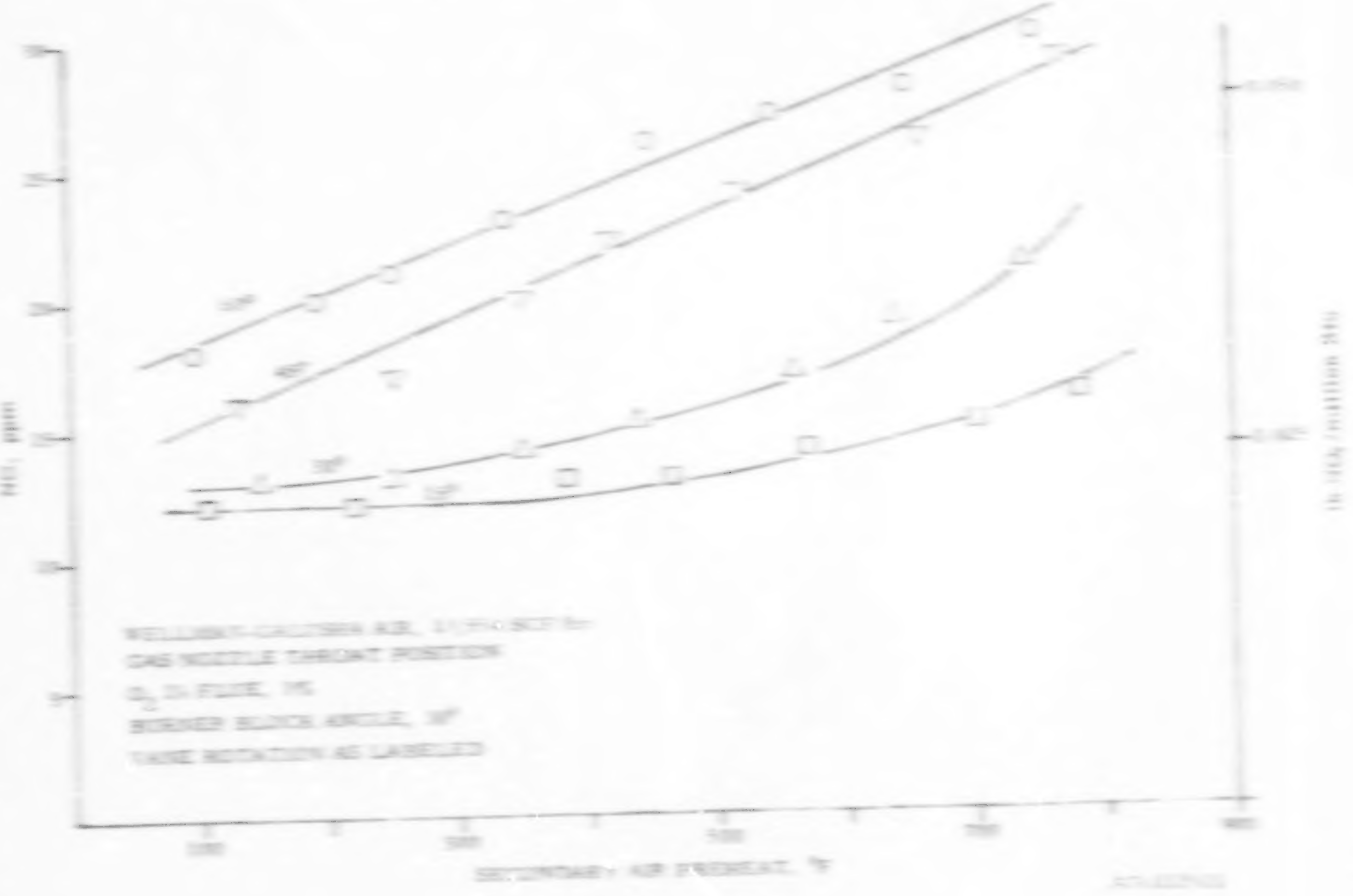


Figure 25. NO versus secondary air preheat with Wellman-Galusha air gas

The NO emission data for Winkler air are presented in Figure 26. As the low adiabatic flame temperature would predict, the NO concentrations in the flue are the lowest of all the gases. The emissions are 82% to 97% lower than those measured for natural gas and show an even more gradual, nearly linear increase with combustion-air temperature.

The NO data for Wellman-Galusha air show a systematic increase in emissions with increased vane angle. This same relationship is not seen with Winkler air. The 15, 45, and 60-degree angle data are all within 2 to 3 ppm of each other but are 5 to 6 ppm lower than the 30-degree angle data.

Figure 27 is an Arrhenius plot for the fuel gases tested with the utility burner at a 45-degree vane rotation. The plot, ln(NO) versus reciprocal of the adiabatic flame, yields a linear relationship. Correlating these data to a relationship suggested by Thompson, Brown, and Beer[1] or the formation rate of NO which is of the form:

$$\frac{d(NO)}{dt} = A \exp(-134.7/RT) \tag{5}$$

yields an activation energy of 153 kcal/mol compared with their 134.7. This good agreement suggests that peak temperatures approaching the adiabatic flame temperatures are controlling the rate of NO formation and suggests that the use of adiabatic flame temperature is a good empirical method of predicting NO emissions.

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[1] Thompson, Brown, and Beer, Combust. Flame, 19, 69 (1972).

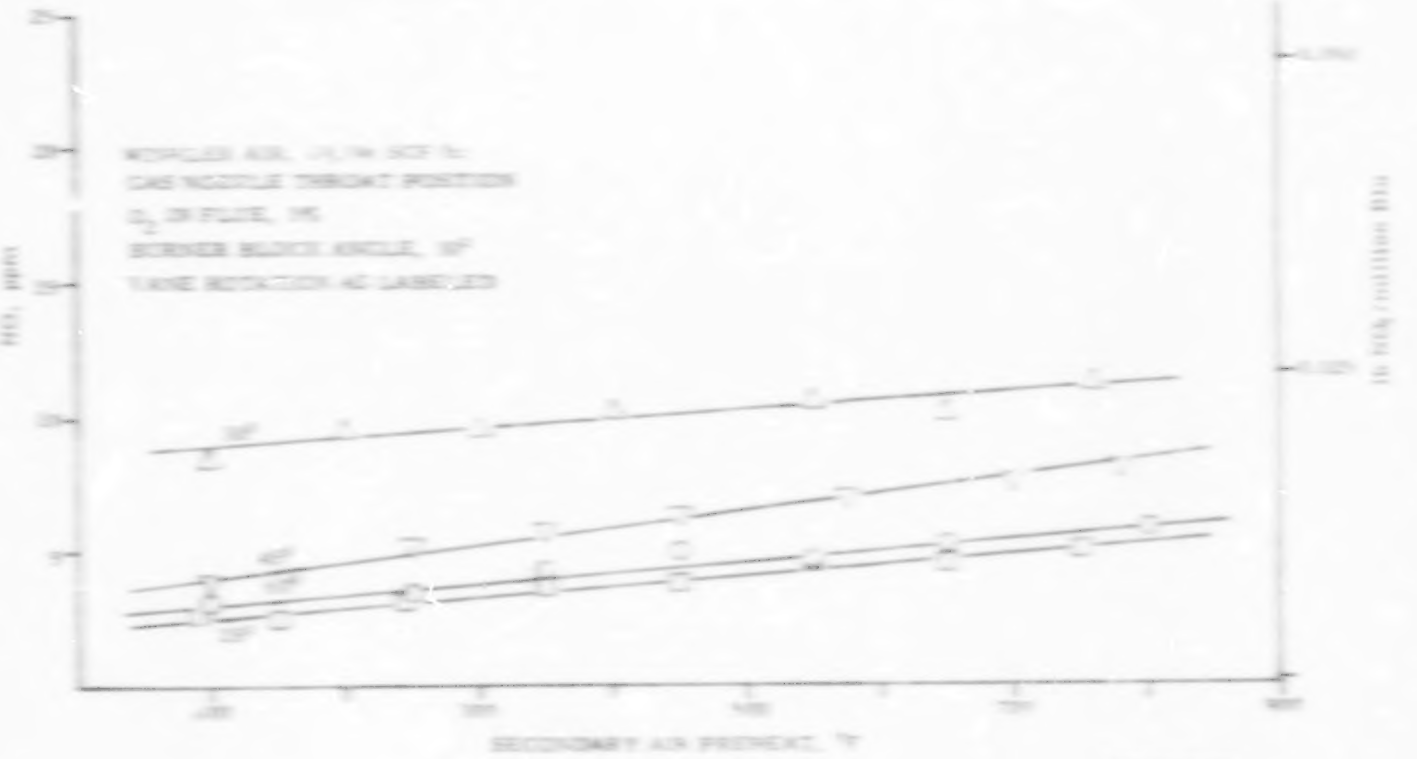

Figure 26. NO versus secondary air preheat with Winkler air gas

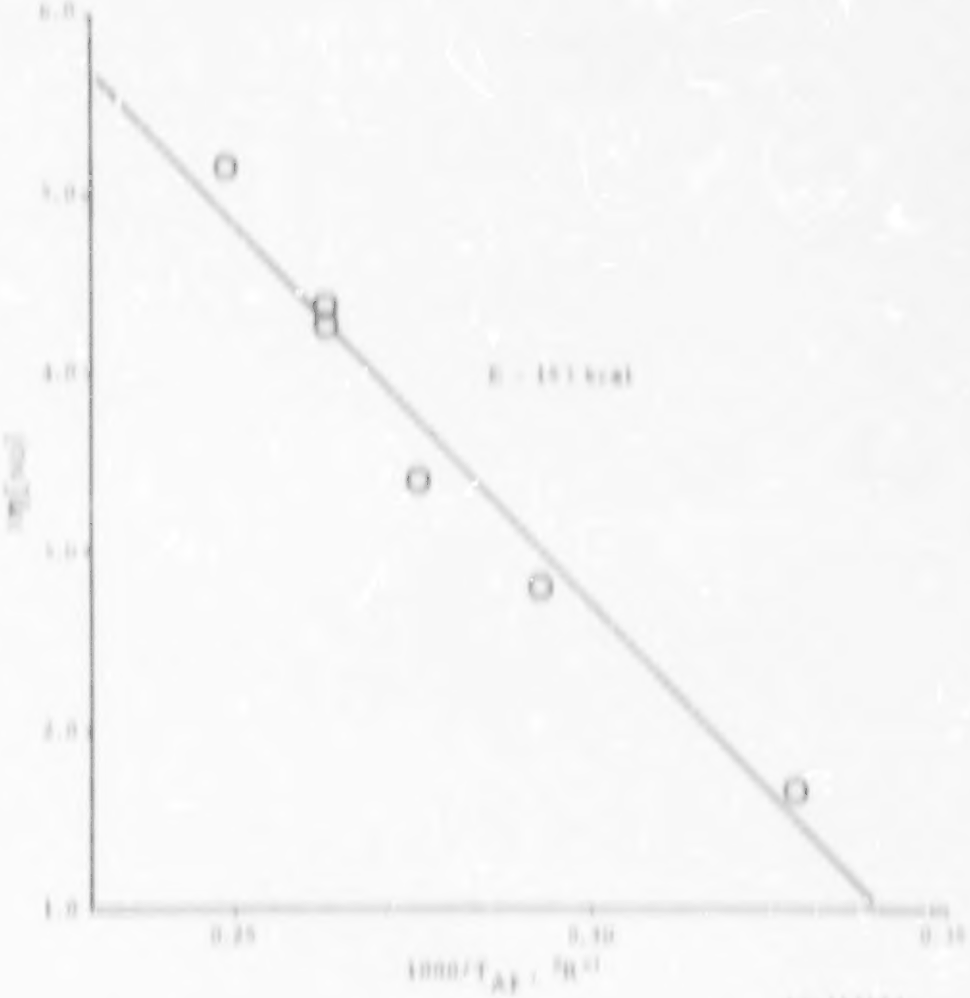

Figure 27. Arrhenius plot of NO versus inverse "pseudo-adiabatic" flame temperature

DATA CORRELATION

NO_x EMISSIONS

Due to the size of the gas-generating system for synthesizing the medium- and low-Btu test gases, the firing density of the pilot-scale test furnace could not exceed 6923 Btu/ft^3·hr. To permit a better correlation as to the level of emissions that could be anticipated from a utility boiler, natural gas was fired with inputs up to 3.75 million Btu/hr. This corresponds to a firing density of 11,538 Btu/ft^3·hr, which produced a NO emission level of 225 ppm compared with the New Source Performance Standard for natural gas at 1000 Btu/SCF of 168 ppm (0.2 pounds NO_2/million Btu heat input). These data are graphed in Figure 28.

A 300-MW utility boiler with a radiant chamber 30 x 60 feet in cross section and 80 feet high is fired with 2.86×10^9 Btu/hr. The firing density for a boiler of this size at this firing rate is 19,860 Btu/ft^3·hr. Extrapolating the data of Figure 28 yields a NO emission level for the 19,860 Btu/ft^3·hr firing density of 458 ppm. To quantify the anticipated NO emission levels from this 300-MW boiler for each of the fuel gases tested, it is assumed that an identical firing density-to-NO emission level relationship would occur for each medium- and low-Btu gas as is represented for natural gas in Figure 28. From this assumption, the NO emission levels presented in Table 5 were projected.

Thus, there were only two fuel gases tested that could comply with the 168-ppm performance standard with the burner system operating normally. Both of the fuel gases (Wellman-Galusha air and Winkler air) that comply with the standard do so because of their low adiabatic flame temperatures, 389° and 758°F, respectively, below the natural gas adiabatic flame temperature. All medium-Btu gases that have adiabatic flame temperatures near that of natural gas would require modifications to the burner/boiler system in order to comply with the performance standards.

CORRELATING FURNACE PERFORMANCE

The efficiencies evaluated on the pilot-scale furnace for each of the fuels tested are listed in Table 6. These efficiencies (defined the same as previously for the boiler, that is, the fraction of the total input enthalpy given up in the furnace by the combustion products) can be evaluated using the flue gas temperatures in

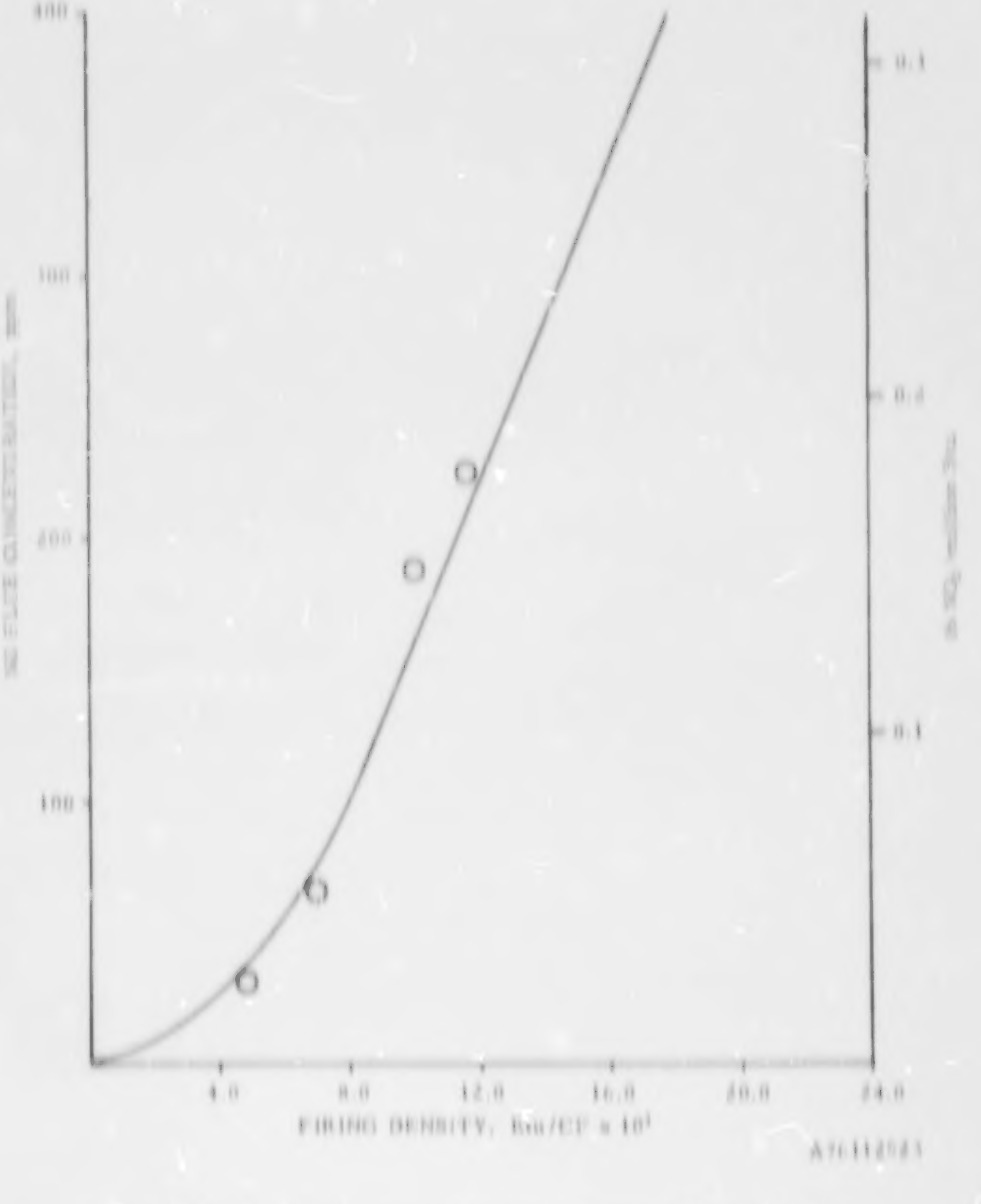

Figure 28. NO flue concentration versus firing density

Table 5. PROJECTED NO_x EMISSION LEVELS FOR A UTILITY BOILER

Fuel	NO_x, ppm	lb $NO_2/10^6$ Btu
Natural gas	458	0.714
Lurgi oxygen	225	0.353
Koppers-Totzek oxygen	733	1.019
Winkler oxygen	514	0.766
Wellman-Galusha air	106	0.198
Winkler air	28	0.061

Table 6. TEST FURNACE EFFICIENCIES AND COMBUSTION PRODUCT PROPERTIES AT THE FLUE

Fuel	η[a]	T_{flue}, °F[b]	$\dot{m}$, SCF[c]	$\dot{Q}$, Btu/hr[d]
Natural gas	28.6	2553	26,639	1,693,083
Lurgi oxygen	23.2	2442	26,883	1,762,337
Winkler oxygen	26.4	2523	25,481	1,730,291
Koppers-Totzek oxygen	33.1	2554	24,236	1,570,836
Wellman-Galusha air	19.0	2434	32,889	1,910,009
Winkler air	10.8	2335	37,919	2,104,174

[a] Efficiency measured for pilot-scale test furnace

[b] Temperature of combustion products at the flue

[c] Volume of combustion products at 60°F

[d] Heat content of combustion products at listed temperature

Table 6 and the combustion products in Table 1. Subtracting the flue gas enthalpy from the total enthalpy input gives the amount of heat transferred in the furnace, and dividing by the total enthalpy input gives the efficiency. The efficiencies evaluated for natural gas and the oxygen produced low-Btu test gases (Winkler oxygen, Koppers-Totzek oxygen, and Lurgi oxygen) are comparable within a range of 25% to 33%. For Wellman-Galusha air with a 160 Btu/CF heating value, the efficiency decreased to 19.0%. The lowest efficiency measured was 10.8%, for Winkler air with a 116 Btu/ft^3 heating value.

In addition to changes in the furnace efficiency when natural gas is replaced with a low-Btu gas, the temperature and volume of combustion gas products entering the convective section will determine the amount of heat absorbed. Using Table 6 to compare the volume of combustion products for the test fuels reveals that Koppers-Totzek oxygen has a 9% smaller volume of combustion products than natural gas, while Winkler air produces a 47% greater volume of combustion products than natural gas. These changes in combustion-product volume will result in changes in gas velocities and will shift the heat absorption pattern within the convective section.

To evaluate a shift in heat absorption when retrofitting a boiler with low-Btu gas requires a method of calculation. Babcock and Wilcox Co. (B&W) agreed to take our experimental data and use them for the input conditions to the convective section to predict differences in overall boiler efficiency (radiant plus convective) between natural gas and low-Btu gases. The method of calculation employed by B&W was to use their design computer program to forecast changes in boiler performance when retrofit with a low-Btu fuel gas.

The particular boiler selected for their calculations was a standard design with a maximum rated steam flow of 2,430,500 lb/hr at 2620 psig/1005°F at the superheater outlet when fired with natural gas. The unit (B&W Contract RB-455) is installed at the Teche Station of the Central Louisiana Electric Co. and supplies steam to a Westinghouse turbine having a maximum capacity of 361 MW. This same unit was reported on by B&W for EPRI Project 265-2, entitled "Low Btu Gas Study," a program designed to look at retrofitting boilers using only existing design information.

To update these results, the flue gas temperatures and gas compositions measured on the IGT furnace were used as input data. These temperatures and gas compositions were assumed to be identical to those entering the convective section of the boiler. Using these experimental results, B&W calculated unit efficiencies for natural gas, Winkler oxygen, and Winkler air fuel gases. The total required output of Unit RB-455 based on a 2,198,000 lb/hr mainsteam flow is 2652.5 X 10^6 Btu/hr. Based on the experimental data and fuel analysis presented in Table 1, B&W generated the information in Table 7. The first line shows natural gas firing with the amount of excess air that the unit was designed for at this load. The second line shows natural gas firing with input conditions (325°F air preheat and 3% excess oxygen) identical to those used for the pilot-scale test furnace. The actual output from firing natural gas with the increased level of excess air is in excess of 2652.5 X 10^6 Btu/hr. This is because higher gas weights result from the increased volume of combustion air creating an overabsorption in the reheater. Similar reheat overabsorption occurs in the output for Winkler air, which is also greater than 2652.5 X 10^6 Btu.

Table 7. B&W CALCULATED BOILER EFFICIENCES USING IGT DATA

Fuel	IGT flue gas temp, °F	Actual unit output, 10^6 Btu/hr	Unit efficiency, %	O_2 in flue gas, % by vol	B&W furnace exit gas temp, °F
Natural gas	--	2652.5	85.1	1.1	2702
Natural gas	2553	> 2652.5	84.8	3.0	2633
Winkler oxygen	2523	2652.5	84.4	3.0	2583
Winkler air	2335	> 2652.5	80.4	3.0	2397

It should be noted that these calculations in no way imply that this, or any other unit, could economically be retrofitted to burn these test fuels. Several other factors in addition to unit efficiency must be considered in an actual retrofit study. Two of these important factors are: 1) redistribution of heat absorption between boiler, primary and secondary superheater, and reheat and economizer surface (a significant redistribution of which will affect metal temperatures, spray flows, and circulation); and, 2) changes in combustion-air and flue gas weight from the original design quantities, which will affect fan and air heater performance. Both of these factors can have a significant influence on the feasibility of retrofitting existing units designed for conventional fossil fuel firing.

To aid in determining the value of the experimental data, B&W reran their design calculation without using the experimental results as input. The new inputs required for the computer program were the fuel composition and the desired temperature of combustion products leaving the air heater. The results of these calculations for the gas temperature and emissivity at the exit of the radiant furnace section are listed in Table 8. The combustion-products temperature leaving the radiant section show excellent agreement with the experimental values. This provides substantiation on how realistically the pilot-scale test furnace was able to model the radiant section of a utility boiler.

Table 8. CALCULATED AND MEASURED EFFICIENCIES AND GAS EMISSIVITIES

Fuel	IGT[a]		B&W[b]	
	T_g	ϵ_g	T_g	ϵ_g
Natural gas	2553	0.18	2613	0.29
Lurgi oxygen	2442	0.19	--	--
Winkler oxygen	2523	0.22	2583	0.35
Koppers-Totzek oxygen	2554	0.19	--	--
Wellman-Galusha air	2034	0.19	--	--
Winkler air	2335	0.17	2397	0.31

[a] Experimental data collected on pilot-scale test furnace.

[b] Calculated values based on normal design technique.

Comparing the gas emissivities of the combustion products at the radiant section exit as measured by IGT to those calculated by B&W reveals a large difference. This difference can be understood by looking at the emissivities dependent variables. These variables are the partial pressure of the radiating gas, the temperature of the gas mixture, and the distance across (beam length) the radiating gas.

The temperature and partial pressure of the radiating gases are similar for the IGT test data and the B&W calculated values. Therefore the difference between the pilot-scale furnace and the 360-MW boiler is due to the different beam lengths, 4 feet and 22 feet, respectively. To directly compare the experimental to the calculated emissivity would require knowing the dependence of emissivity on path length. Adjusting the B&W calculated emissivity to the beam length of the test furnace was not practical because B&W does not use a publicized calculation technique for evaluating emissivities but has developed a semi-empirical method based on years of building and measuring heat absorption rates within the radiant boiler section. On the other hand, the width of the test furnace was fixed, thus negating the possibility of experimentally quantifying the dependence of emissivity on beam length. However, since the only difference between the IGT measured and B&W calculated emissivities is the beam length (products of combustion and furnace exit temperatures are similar), a graphical development of the relationship between emissivity and beam length is possible. This relationship is generated using the zero-zero data point (zero emissivity at zero path length), the IGT measured emissivity, and the semi-empirical emissivity of B&W. The resulting curve for natural gas is presented in Figure 29 and is labeled experimental. Also shown in this figure are relationships between the calculation technique of Hottel and Sarofim and the technique of Leckner.

As the plot shows, the calculated values are approximately proportional to the square root of the mean beam length. Leckner developed a statistical model based on existing spectral data to evaluate total emissivities of carbon dioxide and water vapor in homogeneous gases. For carbon dioxide emissivity, there is good agreement with Hottel's emissivities; however, for water vapor, Leckner's emissivities at temperatures above 1650°F are consistently higher and show that the partial pressure correction factor is temperature-dependent. The measured emissivity lies between the two theoretical curves presented. At the larger path lengths comparable to utility boilers, the experimental curve drops below both theoretical curves.

Similar graphs have been developed showing the relationship of emissivity and the square root of mean beam path length for Winkler oxygen and Winkler air fuel gases. These graphs are presented in Figures 30 and 31. Conclusions similar to those with natural gas can be drawn; the measured emissivity lies between the

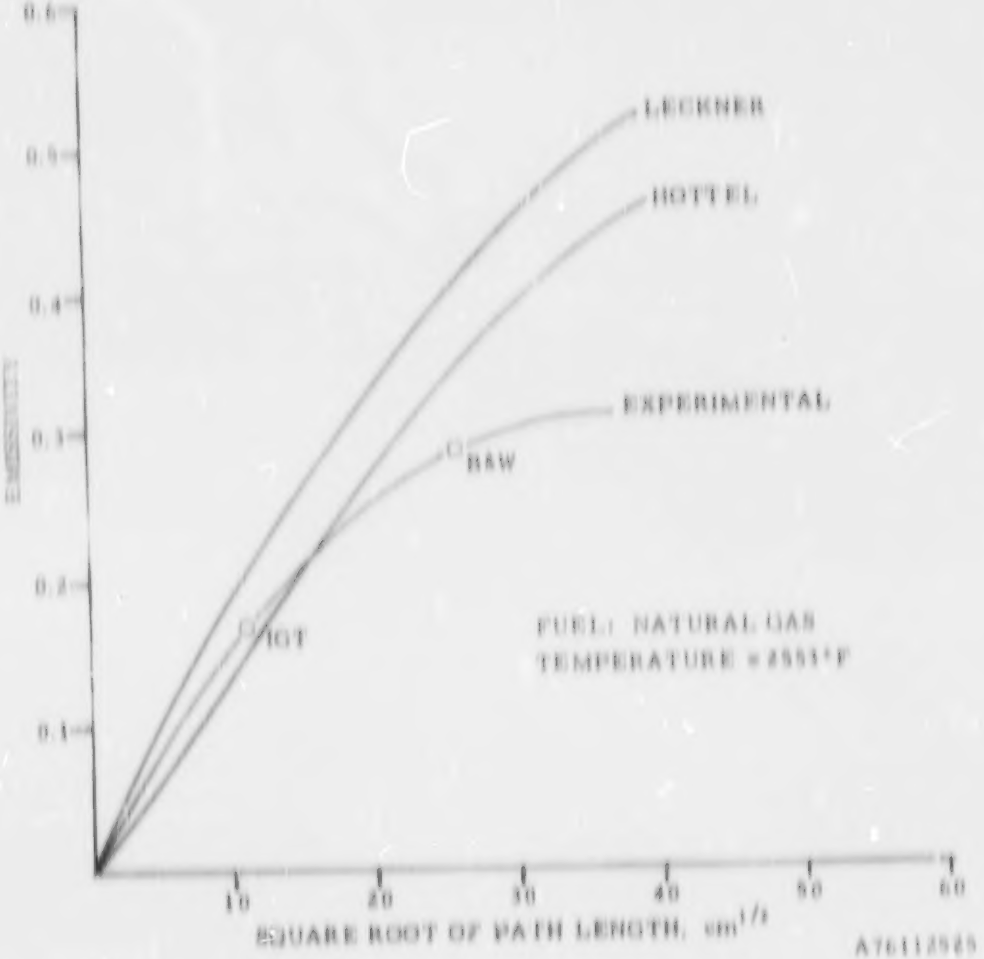

Figure 29. Plot of emissivity versus square root of path length for natural gas

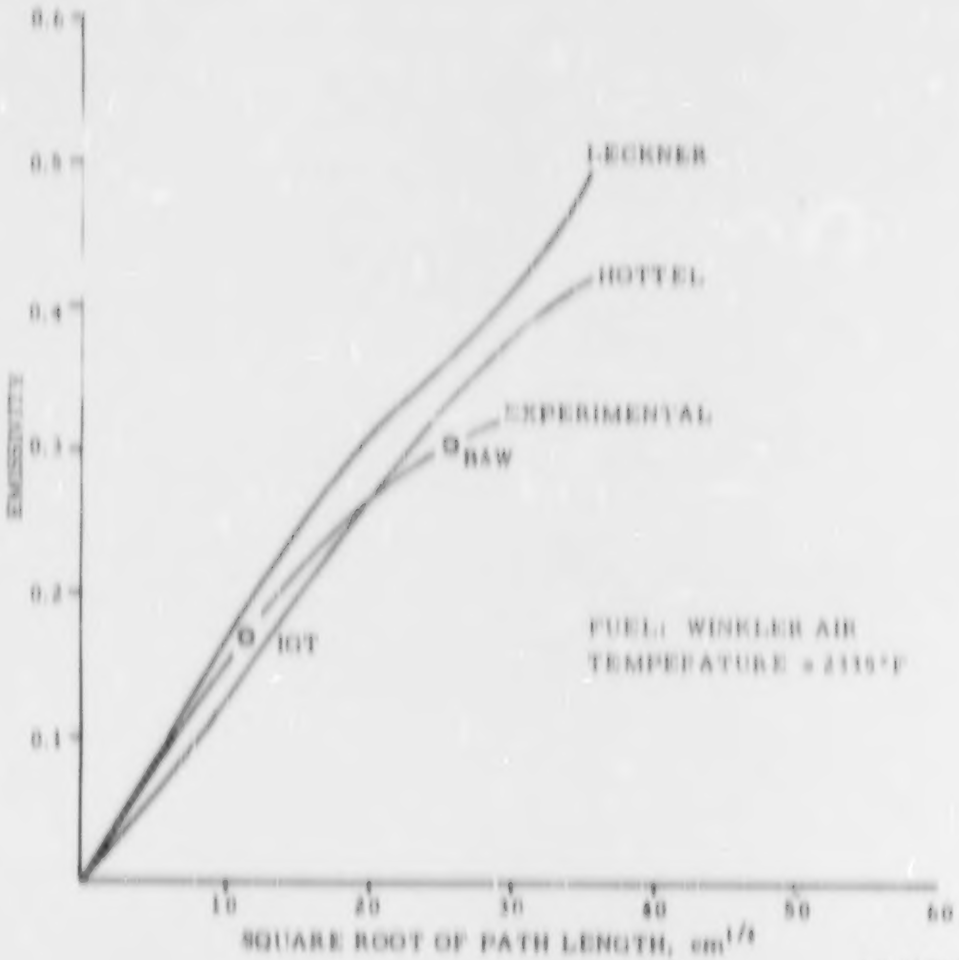

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Figure 30, Plot of emissivity versus square root of path length for Winkler air

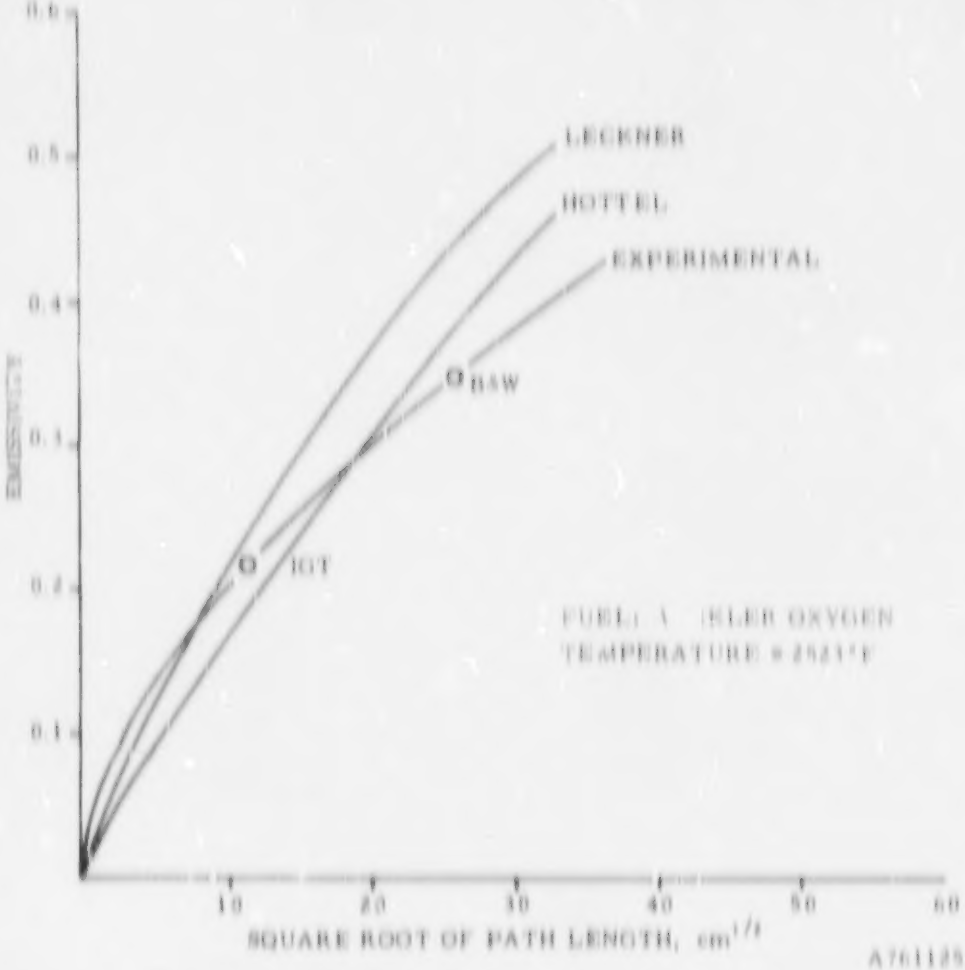

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Figure 11. Plot of emissivity versus square root of path length for Winkler oxygen

theoretical curves, while the semi-empirical data point lies below both theoretical curves. These curves provide a means of estimating the emissivity of nonluminous combustion products with CO_2/H_2O ratios between 0.5 and 1.8. However, these results are very restrictive because they apply only to the temperatures for which the calculations were made. However, as stated previously, these temperatures, approximately 2500°F, are comparable with those found at the exit of the furnace (radiant section) in a utility boiler.

ENVIRONMENTAL ASSESSMENT OF AFTERBURNER COMBUSTION SYSTEMS

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ABSTRACT

This research program was initiated with the overall objective of assessing the performance of afterburner emission control devices by evaluating (1) the potential of afterburners for reducing emissions; (2) the potential for afterburners to generate emissions; and (3) the efficient utilization of fuel in afterburners, as it relates to emission control.

The program is divided into two phases. Phase I includes the utilization of available data (from the literature, from EPA source tests, from state and local agency data, etc.) to update afterburner technology, to determine emissions from afterburners, to determine the effectiveness of afterburners for destroying pollutants in the inlet stream, and to relate the emissions control effectiveness of afterburners to their fuel consumption.

Phase II consists of 4 tasks: two that are directed at generating new data on afterburner performance, and two that are directed at documenting the environmental and engineering aspects of afterburner application. The experimental tasks directed toward obtaining new afterburner performance data in the field and the laboratory, respectively.

The final two tasks consist of utilizing the data generated in the experimental program to complete the environmental assessment of afterburners begun in Phase I, and of developing a "Standard Practice Manual". The manual will assist engineers in deciding when afterburners should be used, which types of afterburners are best suited to specific applications, and what should the design criteria be (in terms of emissions, afterburner efficiency, required temperatures, fuel requirements, etc.).

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INTRODUCTION

Afterburner combustion devices are of interest to the Environmental Protection Agency both (1) because of their use as an emission control device and (2) because of their potential for generating emissions.

Considering the emission control aspect of afterburners, millions of tons per year of hydrocarbon/organic emissions are discharged by a wide variety of industrial processes. The National Inventory of Air Pollutants Emissions - 1968(1), credits industrial processes with emitting 4.6 x 10^6 tons/year of hydrocarbons, 14.4 percent of the national total.

Many of the hydrocarbons and/or organic compounds emitted by industrial sources have been considered as major contributors to photochemical smog, and some hydrocarbons/organics may be harmful (e.g., toxic or carcinogenic) in themselves. Other aspects of hydrocarbon/organic emissions include the odor associated with many such compounds and where emission levels are high, the possibility of the occurrence of dangerous local concentrations of combustibles. Consequently, afterburners have been used for many years and in a variety of industries to minimize these problems by reducing emissions of combustible and/or organic gases and vapors.

The second aspect of afterburners concerns their potential for generating pollutants. Polycyclic organic matter (POM) has become of considerable concern as a pollutant since some compounds that fall within this broad category have been identified as carcinogenic. Because POM compounds are the result of incomplete combustion, it is generally recognized that poor combustion conditions (low temperature combustion, poor mixing, quenching) are contributors to POM formation and emissions. It is fairly obvious that afterburners, that are designed or operated in the most "economical" manner (that is, using minimum energy for mixing and minimum fuel to raise temperature), have a potential for having the necessary poor combustion conditions to generate POM. In a similar manner,

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aldehyde emissions may be generated in afterburners. Also, catalytic afterburners may emit trace quantities of catalytic surface materials through the action of erosion associated with thermal cycling, corrosion, and abrasion.

A more recent concern regarding afterburners involves their fuel or energy consumption. Most afterburners are gas fired and, with curtailments of natural gas usage by industry, the ability to operate afterburners on alternate fuels (specially fuel oil) becomes an issue. Also, the heat released in the afterburner is frequently lost -- no attempt is made to utilize this energy. As the cost of energy increases, greater efforts at recovering the heat released in afterburners must be considered.

Unfortunately, afterburners have never been the subject of a broad-based and systematic experimental study to evaluate their overall performance in such areas as (1) Emission control; (2) Pollutant generation; (3) Effective fuel use. Brief discussions on afterburners appear in the Air Pollution Engineering Manual[2] and in the EPA Control Technique Document[3]. In the 1970-1972 period, EPA sponsored an "Afterburner System Study". This study included a comprehensive review of the literature concering afterburners and contacts with industry representatives. The report on that study[4] was an impressive document, but the authors had to conclude that there were major gaps in the available data. Thus, they recommended various levels of further research efforts to fill these gaps.

Through the present contract, EPA is seeking to update the previous study to: (1) consider developments in afterburner technology since completion of that study; (2) expand on emissions control and generation aspects to include the latest EPA methodology for Level I, Level II, and Level III emissions measurement; (3) consider energy aspects including alternate fuels and waste heat recovery; and (4) conduct experimental field and laboratory programs to fill gaps that still exist in the knowledge of afterburner performance as it pertains to emissions and efficiency. Products of the proposed study will include: (1) An environmental assessment of afterburners as control devices. (2) An environmental assessment of afterburners as pollutant generators. (3) A Standard Practice Manual to guide application engineers, potential users, afterburner manufacturers, and installers to the best technology for applying afterburners control devices.

It should be reemphasized that, in addition to the environmental aspects of afterburner designs and applications, energy considerations are included as an important part of this study. This study recognizes that effective fuel utilization must be an important part of our national and industrial decision making process.

AFTERBURNER TECHNOLOGY

TYPES OF AFTERBURNERS

Five different basic types of afterburners can be defined as follows:

(1) Direct flame combustion afterburners
(2) Thermal combustion afterburners
(3) Catalytic afterburners
(4) Flares
(5) Boilers, process furnaces, and heat recovery furnaces.

The first four types are primarily used for pollutant destruction and (except for flares) may or may not include waste heat recovery. The last type usually is designed for recovery of thermal energy from the fuel value in the gas stream and pollutant destruction may be a secondary consideration.

Direct flame combustion afterburners and thermal combustion afterburners are similar. Both provide for the destruction of combustible (or oxidizable) species in a hot, oxidizing environment. The basic difference is that the direct flame afterburners provide for destruction of the combustible species by passing the gas stream through a flame while the thermal combustion afterburner destroy the combustible species by exposure to a high temperature-non flame environment for the required residence time to achieve the necessary oxidation reactions. The thermal combustion afterburner may have a flame, but the flame serves only as a preheater. Both the direct flame and thermal combustion afterburners will usually require the use of auxiliary fuel to create the flame environment or supply preheat energy, respectively. Both afterburner types generally are operated at temperatures of 540 C to 815 C (1000 F to 1500 F).

The catalytic afterburner provides a catalytic surface on which the combustible species are oxidized at temperature of about 370 C to 480 C, (700 F to 900 F). Because the heat released by oxidization of combustibles in the carrier gas stream may not be sufficient to maintain the catalyst temperature, additional thermal energy may be required to maintain the catalyst temperature. This additional energy may be in the form of preheating of the carrier gas stream, or may involve adding fuel to the carrier stream to increase the heat release rate at the catalyst surface. Because lower temperatures are required in catalytic afterburners (and heat losses should be lower), the auxiliary fuel requirements of catalytic afterburners should be less than for the previously mentioned types.

Flares are essentially afterburners with an unconfined flame and exhaust gas stream. They generally require some mechanism to promote mixing and may require the use of auxiliary fuel or continuous ignition to insure a constant flame. Because of their unconfined nature, flares are less well controlled than other types of combustion afterburners; that is, mixing, reaction time, quenching, time-temperature patterns, etc., are not nearly so well controlled in flares as in confined afterburners. Hence, emissions of incompletely oxidized species may be higher than for confined afterburners. Also, because the nature exhaust stream from a flare is not confined, it is difficult to measure pollutant emissions from these units.

Boilers, process furnaces, and heat recovery furnaces are afterburning devices used to recover the energy content of the combustible in gas streams where the energy content is sufficiently high and sufficiently constant with time to justify the investment in the boiler or furnace. For example, refineries use off gases from the catalyst regenerator (associated with catalytic cracking plants) to fire CO boilers to generate steam. Also, blast furuace gases (with heating valves of 50 to 100 Btu/scf) are fired in blast furnace stoves.

The scope of work for the present program dictates that the major effort be directed towards the first three types of afterburners listed above. However, because of similarities between afterburner and flares, during the Phase I activity we will give some attention to flares.

There are major difference between afterburners and equipment and processes for utilizing the fuel heating valve in waste gases. This fact, together with our knowledge that EPA has other programs on industrial boilers and industrial process furnaces, has lead us to exclude these areas from consideration in our study.

PERSPECTIVE ON AFTERBURNER DESIGN AND APPLICATION PROBLEMS

Afterburner pollution control systems are used to reduce combustible pollutants carried by exhaust gas streams by incineration, frequently with an auxiliary fuel. The pollutants may include gases, vapors, and aerosols. The afterburner functions by exposing the pollutant to a combination of circumstances, involving oxygen concentration, temperature, and in catalytic units a catalytic surface, which lead to the destruction of the pollutant. Ideally, the pollutants are reduced to simple chemical compounds (CO_2 and H_2O) having no pollution potential.

While this ideal should be achievable if the pollutants are subjected to a sufficiently high temperature for an adequate residence time and in the presence of oxygen, economic and engineering factors have currently restricted the operating temperature of afterburners to less than 2000 F, commonly to the range of 1500 F and below. Afterburners employing catalysts are frequently restricted to still lower maximum temperatures.

Under these conditions of only moderate temperatures, mixing of the pollutant-carrying stream with the combustion gases from the auxiliary fuel becomes extremely important; if poor mixing exists, a portion of the pollutant will escape the intended oxidation environment, or be exposed for less than the intended time. The result will be emissions of unoxidized or partially oxidized species, such as aldehydes, which may be more objectionable than the original hydrocarbons.

Although there appears to be a limited amount of well-documented information available concerning the conditions of temperature, oxygen concentration, and duration of exposure required to destroy specific pollutants (5-10), information on the mixing efficiency in typical afterburner geometries is largely lacking. As a result, most afterburners appear to be designed by "rules of thumb" and empirical tests. Consequently, some afterburner installations actual result in the outlet stream containing more pollutant gas than the inlet stream(11). Deficiencies in performance of an installed unit are generally corrected by increasing the auxiliary fuel input and, thus, the general temperature level. Obviously, afterburner efficiency decreases when this type of a "fix" is used.

Catalytic afterburners are generally employed to take advantage of the lower temperature level (and correspondingly lower auxiliary fuel requirement) needed to achieve rapid oxidation of hydrocarbons in the gas stream when a catalyst is present. However, catalytic afterburners can only be applied to "clean" pollutant streams, ones that will neither poison nor blind the catalyst, and they usually cannot be applied sucessfully to gas streams containing particulate. Additionally, catalytic units may be particularly prone to only partially oxidizing come types of pollutants. The resultant oxygenated species (aldehydes) may have a greated pollutant potential than that of the original material.

Complicating the problem of afterburner design and operation is the fact that afterburners are used in a wide variety of industrial processes. The following is a partial listing of equipment processes and industries using afterburners:

Resin kettles
Varnish cookers
Sulfuric acid manufacturing
Phosphoric acid manufacturing
Paint-bake ovens
Wire-coating process
Soap and synthetic
  detergent industries
Glass manufacture
Frit Smelters
Food Processing Equipment
Fish canneries
Animal-matter rendering
Electroplating
Insecticide manufacture
Oil and solvent refining
Chemical milling
Coffee roasting
Meat smokehouses
Fertilizer plants
Rotogravuring
Degreasing operations
Dry cleaning
Fiberboard drying and curing

With afterburners being applied to such a wide variety of processes and industries, it is doubtful that available performance data are used to the maximum in ensuring good design and application. Generally, a particular industry will follow "industry practice" and not take full advantage of the opportunity to develop generic or broadly applicable data for design. Also they may not fully recognize or exploit the fact that pertinent design and application data exist for units serving different industries but handling similar pollutants, carrier gases, etc. The use of generic afterburners criteria (as discussed later) will maximize the usefulness of existing and new data and will provide a common basis for discussion and interchange of data among users and manufacturers.

PERSPECTIVE ON AFTERBURNER OPERATION

When viewed strictly as a piece of equipment, rather than as a process, afterburners are subject to all of the troubles and problems of any combustion device, and these may be magnified by the fact that the afterburner is an auxiliary device and, thus, may not receive necessary attention and maintenance. Improper operation of controls, durability of refractories and other high temperature components, corrosion, and other similar problems may be encountered in operating units.

AFTERBURNER RESEARCH PROGRAM

PROGRAM OVERVIEW

Phase I of the current study is directed toward effective utilization of all available data and technology relating to afterburners. Thus, an important part of the Phase I effort is to determine and document what is known and unknown about afterburner performance. The final step in Phase I will include the preparation of detailed recommendations for R and D on afterburner control systems that will be conducted as part of the Phase II effort.

Phase II of the current program will include experimental research to fill voids in available data. It will include field studies of operating units and laboratory studies (under more conditions) of afterburner performance.

PHASE I - PROBLEM ANALYSIS

Phase I consists of the Problem Analysis phase of the program. It includes: Research Plan Preparation, Technology Review, Comprehensive Emissions and Performance Analysis, and Preliminary Environmental Assessment. Each of these is discussed separately below.

Research Plan Preparation

The *Afterburner Systems Study* report[4] included a section on research recommendations. The basis for those recommendations was to "generate the data required to predict and improve process performance and economics and extend the application of afterburners to additional air pollution sources". Those research recommendations are primarily afterburner-design oriented (including development of new afterburner designs) and give less attention to afterburner application.

The basic purpose of the present program concerns the application of afterburners, and specifically an environmental assessment of afterburners as pollution control systems. Other important aspects relating to afterburner application include energy use and economics. Thus, it is necessary to review and revise the research plan contained in the *Afterburner Systems Study* to generate a plan compatible with the overall interest of this EPA program. Certain aspects of the earlier program will likely remain as important aspects of the new research plan, although they might be modified in detail to place emphasis on obtaining emissions data. Thus, laboratory and field tests would likely be included in the new plan, but they would be extended to include Level I and Level II sampling and analysis. The design oriented aspects of the former research plan probably would be deleted as not required to meet the objectives of the present program (although it is acknowledged that these aspects may provide data useful to the overall development of afterburner technology). Research areas that might be deleted include "afterburner gun (burner) and control system development" and "new catalyst development". Mathematical modelling of afterburners will probably not be recommended as it pertains to detailed afterburner design. However, some modelling of input-output relationships may be useful in developing application guidelines for the manual.

Technology Review

The Technology Review consists of reviewing the present technology concerning afterburner control systems and compiling background information to support the environmental assessment.

The report of the previous study, *Afterburner Systems Study*, includes a 17 chapter "Afterburner Handbook". This handbook section compiles much of the technology regarding afterburner design and operation. In the conduct of this task, Battelle is updating afterburner technology as described in the earlier report. To perform this updating, Battelle is reviewing new technical literature concerning afterburners (published since the earlier study) and is working with IGCI and other industrial contacts (as subcontractors and consultants, and through industry committees and trade associations) to review the previous material and insure that the technology described is current.

One area that appears to require more extensive treatment than it received in the previous study is afterburner application. In the *Afterburner Systems Study*, afterburner application was primarily limited to part of two chapters, whereas afterburner construction details were discussed extensively in at least seven chapters. The present program is weighted more heavily in the application area. Therefore, Battelle is limiting its effort with regard to afterburner design details to an updating of the previous study, but is expanding upon the areas of afterburner application.

Battelle is approaching the afterburner application technology by generic categories and not by cataloging of industry-by-industry details. Several generic categories that are being used in evaluating afterburner technology include:

(1) Type of device (direct combustion, thermal, catalytic)
(2) Carrier media composition (air, flue gas, inert gas, etc.)
(3) Carrier physical conditions (temperature, pressure, etc.)
(4) Carrier pollutant type (organic, ash, trace compounds, etc.)
(5) Afterburner supplemental fuel (gas, oil, waste gas, etc.)
(6) Carrier gas combustibles content.

An additional advantage of using generic categorization of afterburner applications is the protection of proprietary industrial data. Because of the nature of some industries, emission characterization and concentration data may disclose proprietary details about processes or production rates. Thus, by not reporting data by plant name, location, or specific process, but generically, the proprietary interest of the plant operators is protected and we will be more likely to receive cooperation in making data available and granting permission for testing.

Mathematical Modelling--

As part of this effort, we plan to develop simple parametric models representing generalized versions of both thermal and catalytic afterburner systems. The availability of these models will be important for correlating the present data on afterburner systems, for the logical development of methods for predicting and improving afterburner performance, for the planning and analysis of the results from the laboratory and field tests, and in the development of mathematical relations of afterburner performance for the manual.

These models are intended to take into account the parametric interactions among the flow processes, the chemical processes, and the thermal processes. Idealized mechanisms will be assumed for the various parameters in each type of process. The chemical processes will be represented by global and not detailed chemical-kinetic mechanisms. The different processes in the models will be coupled in such a way mathematically so that individual processes can be modified or extended, if necessary, without affecting the other processes in the model. Final output from these models will be prediction of pollutant concentrations as a function of input and operating parameters.

Comprehensive Emissions and Performance Analysis

The Comprehensive Emissions and Performance Analysis consists of the development of estimates of the effectiveness (efficiency) of afterburners for reducing pollutant emissions and the levels of emissions from afterburner systems. The scope of this task includes all emissions from afterburners. Three categories of emissions are being considered:

(1) Pollutants that pass through the afterburner and are unaffected, either because the afterburner does not control these emissions (e.g., SO_2), or because the afterburner is not 100 percent efficient (e.g., trace emissions of input hydrocarbons).

(2) Pollutants that are altered or manufactured within the afterburner by chemical reaction (e.g., aldehydes and POM formation due to "poor" combustion conditions and conversion of SO_2 to SO_3 or sulfates).

(3) Pollutants that are released from the afterburner itself (e.g., trace metals eroding from catalytic combustors).

The present effort is limited to the utilization of available emissions data and does not involve field sampling. (Field sampling is included in Phase II.)

Although the present effort does not involve field sampling, the EPA sampling and analysis philosophy is being kept in mind while collecting the available emissions data. Thus, as data are assembled, judgements are being made as to whether the data are of Level I, Level II, or Level III quality, both from the viewpoint of completeness and accuracy.

Information sources that are being utilized will include:

(1) EPA sampling test reports - New Source Performance Standards programs (for example Battelle has sampled afterburners at asphalt roofing plants under the NSPS programs)

(2) State and local agency sampling test reports
(3) Afterburner manufacturer's tests (several particularly impressive research programs have been conducted by Surface Combustion and reported by Hemsath, et al[5-9]).

Preliminary Environmental Assessment

The culmination of Phase I will be the preparation of a Preliminary Environmental Assessment. While it is expected that the data obtained in Phase I will not permit a comprehensive environmental assessment to be completed, the attempt to complete the environmental assessment will point out the areas where sufficient data are lacking. The success (or lack of success) in completing the environmental assessment at this point will provide direction for the Phase II studies.

Because afterburner combustion systems are air pollution control devices, instead of industrial emission-generating processes, the environmental assessment must be approached in a somewhat different manner than one would use in conducting an environmental assessment of a basic emission source. For one thing, afterburners are used on a wide variety of industrial processes and a conventional environmental assessment would require sufficient study of each of the industrial processes to precisely define plant pollutant output (afterburner pollutant input). Such an approach is beyond the resources available for this program. Thus, we are approaching the environmental assessment from the generic categories discussed above. This approach will recognize important differences between afterburner types, carrier gases, inlet conditions, pollutants, etc., but will limit the assessment to a reasonable number of cases. This approach also will permit extension of the results of this study to the evaluation of the use of afterburners on new processes, where afterburners are not presently being used.

Three criteria relating to acceptable emission levels will be considered when performing the environmental assessment. These criteria are:

(1) Permissible ambient air quality concentrations
(2) Source emission standards
(3) Application of "best available" control technology.

Although a Federal standard exists for ambient levels of hydrocarbons, it is specifically directed to the automobile-smog problem.* Federal ambient standards for hydrocarbon/organics that are directed to industrial process emissions [illegible] not exist, nor do Federal standards exist for source emissions from most "new" industrial processes. Hence, Battelle is conducting a brief evaluation of state standards in these areas. Once the proper background information is available, EPA and Battelle can then agree to a set of values to be used as the "baseline" criteria for the environmental assessment of afterburner systems.

Among the important factors being considered in performing the environmental assessment of afterburners are:

(1) Alternative control systems
  - Are afterburners required or can some other control system be used to control the emissions?
  - What types of afterburner control systems can be used (direct flame, catalytic, etc.)?
  - What is the relative environmental impact of various afterburner types?

(2) Selection of afterburner operating variables
  - What fuels are applicable?
  - What are the temperature and residence time requirements to destroy the pollutant?
  - What are the environmental impacts of the various fuels? The various operating conditions?

(3) What are the environmental impacts of emissions generated by the afterburner?
  - Due to chemical reaction of the emission species?
  - Due to erosion of the afterburner?

(4) What is the effect of nonstandard afterburner operation
  - How are startup, shutdown, and transients handled?
  - What about afterburner malfunction?
  - How easily are the catalysts poisoned?
  - How sensitive are afterburner effectiveness and emissions to input stream variables?

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* The Federal standard is 160 μg nonmethane-hydrocarbons/m^3, or 0.24 ppm/3 hours (6 a.m. to 9 a.m.).

(5) What are the environmental impacts of
  - A well designed (and presumable costlier) system?
  - A more economical (and presumable less effective) system?

(6) What are the areas of needed R&D relating to
  - Afterburner control system design technology?
  - Control system application technology?

EXPERIMENTAL PROGRAM AND FINAL ANALYSIS

Phase II of the Research Program consists of the following:

- New data generation
  - Field testing
  - Laboratory testing
- Analysis and evaluation
  - Environmental assessment
  - Standard practice manual.

Based on Battelle's knowledge of what is known about afterburner technology and afterburner application relative to a comprehensive environment assessment, it is certain that the Phase I environmental assessment will contain numerous gaps. For instance, to the best of our knowledge no thorough emissions tests (even equivalent to Level I) have been conducted on any afterburner systems. Unless ongoing programs show promise of gaining needed information, the completion of a thorough environmental assessment will require the conduct of the field and laboratory programs called for in Phase II. Although the overall program needs are generally well defined at this time, some specific needs will await definition during Phase I and so, to some extent, are being treated in generalities at this time.

Field Testing

Some field testing of afterburner control systems has been done for EPA. For example, under the NSPS program, Battelle conducted a sampling program on the afterburners applied to the blowing still on the Elk Roofing Company asphalt roofing plant in Stevens, Arkansas(12), and on the saturator line at the

Certain-Teed Products asphalt roofing plant at Shakopee, Minnesota(13). Two CO-boiler/afterburner units also have been sampled by Battelle(14-15). It is likely that other afterburner installations have been sampled for EPA and many have been sampled for state and local agencies as part of compliance tests.

However, the sampling that has been conducted to date has not been sufficiently comprehensive to qualify as complete Level I efforts. Generally these sampling programs have been directed toward measurements of specific criteria pollutants (particulates, gaseous hydrocarbons, SO_2, NO_x) and occasionally included certain trace hazardous pollutants (POM, trace metals, sulfates). Other data are lacking; for instance, particle size measurements were attempted on several asphalt roofing plants but were unsuccessful. No attempt has been made to conduct toxicity studies or to broadly classify organics by class. Thus, although the data from these sampling programs are available and will be useful to this program, there are gaps between the available data and complete Level I data.

The field program will be designed to take advantage of the generic classifications defined earlier, thus avoiding unnecessary repetitive sampling at many industries. Basically, the sampling will be built around the EPA Level I sampling and analysis philosophy and methodology. However, it is recognized that Level I sampling and analysis are not adequate to define emissions of certain important pollutants (e.g., specific organic compounds such as aldehydes and POM compounds). Thus, some Level II work will be required.

Laboratory Testing

Although field testing is an excellent method for determining emissions from afterburners and afterburner effectiveness for controlling emissions, field testing is expensive and it may be difficult to locate plants to provide the complete range of desired operating conditions (input emission types, input emission levels, etc.). Therefore, laboratory testing of afterburners and/or afterburner simulation rigs under conditions simulating real afterburner operation may be necessary to obtained needed data.

The use of laboratory testing of afterburners provides a means of studying the effect on emissions of variations in:

(1) Input pollutant types (hydrocarbons, aldehydes, ketones, etc.)

(2) Input pollutant concentrations

(3) Operating conditions (temperature, residence time, etc.)

(4) Carrier gas (oxidizing, reducing, inert, moisture content, etc.)

(5) Afterburner design

(6) Supplement fuel (natural gas, fuel oil, other).

The actual laboratory rig(s) used for these studies might include an optimum or ideal afterburner (to define the limits of what can be accomplished with afterburning) and one or more simulations of commercial afterburners or new afterburner concepts. Measurements that would be made would include at least:

(1) Temperature, pressure drops, air and fuel inputs per unit gas flow, etc., to define the afterburner operating conditions

(2) Input pollutant concentrations with appropriate methods including Level I and Level II methods

(3) Output pollutant concentrations with Level I and Level II sampling and anlysis procedures

(4) Fuel consumption.

Results would be expressed in terms of:

(1) Emissions from the afterburner

  (a) Hydrocarbons

  (b) Oxygenated organics (aldehydes, ketones, esters)

  (c) Criteria pollutants

  (d) Trace metals

  (e) Other

(2) Afterburner effectiveness or efficiency ($\frac{\text{Input} - \text{output}}{\text{Input}}$ x 100)

(3) Pollutant destruction per unit of fuel consumed

(4) Afterburner efficiency as a function of temperature and residence time

(5) Others, as appropriate.

Typical of the laboratory testing that might be conducted is the research performed by Hemsath of Surface Combustion$^{(5-9)}$. Hemsath studied the conditions required to destroy certain hydrocarbons under ideal conditions (thorough mixing, all input carrier gas at minimum required temperature, etc.).

By consulting industry (IGCI and afterburner manufacturers) during the planning and conduct of the laboratory program, Battelle believes that they can insure that the design and operation of the laboratory afterburner rigs representative of industry practice. Thus, we will avoid the possibility of acquiring extensive laboratory data that the industry regards with a skeptical eye.

Final Environmental Assessment

At the conclusion of the experimental program, the data should be available to complete a comprehensive environmental assessment. This environmental assessment will answer questions left unanswered in the Preliminary Environmental Assessment due to gaps in available data.

Standard Practice Manual

To insure the technology transfer from the Battelle staff conducting this study and their [illegible] to the industry (and specifically to those concerned with the application of afterburners), Battelle will prepare a "Standard Practice Manual" on afterburner application. This manual or guideline will present informations on how afterburners can be applied to control emissions from various industrial sources. It will provide step-by-step directions for determining when and how afturburners should be used and for selection of the best afterburner systems for various applications.

A generic approach will be used with regard to afterburner design and pollutant sources. That is, the application of types of afterburners will be presented and the use of specific brand names or mention of manufacturers will be avoided. The generic afterburner types will be as specific as possible and will not be limited to "direct flame" and "catalytic" types. Thus, as far as possible, units with different design approaches will be considered as separate subtypes within the overall "direct flame" and "catalytic" classification.

Likewise, instead of considering each industrial source separately, the generic source categorization described earlier will be used as the basis for describing pollutant input streams. To the extent that data are available (either in the literature, from EPA source tests, from manufacturers and trade associations, or from field testing conducted on this study) specific industrial sources will be categorized within the generic classifications used in this report. Hence, a particular industrial user would have minimum difficulty in considering afterburner application to his specific emissions problems.

A major aspect of this manual will be the material relating afterburner application technology to the meeting of pollutant standards. Prime consideration will be given to meeting emission standards and "best practice" control technology. Because of the almost limitless variety of combinations of industrial sources for which afterburners should be considered and local conditions (other sources, terrain, meteorology, etc.), the meeting of ambient air quality standards will not be treated extensively. It will be presumed that, for most cases, state implementation plans will translate the meeting of ambient standards into acceptable emission values for the specific local situation.

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ADVANCED COMBUSTION SYSTEMS FOR STATIONARY GAS TURBINE ENGINES

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This paper was not received in time for publication, and therefore will be included in Volume V.

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DEVELOPMENT OF EMISSION CONTROLS FOR IC ENGINES

Contract not awarded in time for paper submittal, see Volume V.

EMISSION CHARACTERISTICS OF SMALL STATIONARY DIESEL ENGINES

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This paper was not received in time for publication, and therefore will be included in Volume V.

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SESSION V:

ADVANCED PROCESSES

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CHAIRMAN

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INVESTIGATION OF STAGING PARAMETER FOR NO_x CONTROL IN BOTH WALL AND TANGENTIALLY COAL FIRED BOILERS

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ABSTRACT

Tests on an EPA 1 to 1.5 x 10^6 Btu/hr pilot scale pulverized coal furnace show that NO_x emissions of 100 to 150 ppm (zero percent O_2) are achieveable with the use of two stage combustion. Comparable NO_x emission levels were obtained with three different coal types fired in either the single-wall or tangential configuration. On the basis of those tests, the combustion conditions leading to minimum NO_x appear to be (1) operation of the primary flame zone at 75 to 85 percent of stoichiometric air, (2) complete separation of stage air from the first stage, (3) first stage mean residence time of 3 to 5 seconds, (4) high first stage volumetric heat release rate and/or high first stage combustion air preheat. Additionally, the minimum NO_x condition was achieved using the same burners as were used in uncontrolled operation to simulate full scale equipment.

Tests to date have explored the effects of first and second stage combustion conditions on NO_x production with three types of coal: fired in a five-burner, single-wall configuration, in a four-burner tangential configuration and in a four-burner horizontal tunnel configuration. First stage conditions varied were: stoichiometry; residence time to injection of stage air; volumetric heat release rate; combustion air preheat; and fuel/air mixing (swirl, injector design). Second stage variables were residence time to the convective section, stage air preheat and stage air injector design. Initially, the furnace was operated in the baseline, uncontrolled condition to compare emissions to full-scale equipment. Good simulation of both the level of NO_x emissions and the variation of emissions with excess air was demonstrated for both the wall-fired and tangentially-fired configurations.

The first stage stoichiometry was the most significant variable in NO_x reduction. Emissions of 100 to 150 ppm (zero percent O_2) were achieved at a first stage stoichiometric ratio of 0.75 to 0.85. This corresponds to about

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an 85 percent reduction for the wall-fired configuration and an 80 percent reduction for the tangential configuration. Below 0.8, the NO_x levels were higher presumably due to increased second-stage NO formation. At the 0.8 minimum NO_x condition, the emissions were relatively insensitive to first stage mixing. That is, similar emissions were achieved for both the wall-fired and tangential-fired configurations using several different burner settings and/or injector designs. Operation at a stoichiometric ratio of 0.9 or higher, however, showed a strong effect of first stage mixing. Here, the lowest NO_x was seen for tangential-firing and for wall-firing with the use of a slow-mix axial injector. These results suggest that combined burner modification and staged combustion will yield the best NO_x reduction if operation below a stoichiometric ratio of 0.9 is precluded by operational constraints. In general, increasing the first stage residence time for all configurations decreased NO_x emissions. Staging test and hot sampling in the first stage of the horizontal extension configuration showed that NO decays from high peak levels generated during the first second. This peak is dependent on the stoichiometric ratio of the first stage. Also, for a fixed residence time, increasing the volumetric heat release rate or the combustion air preheat decreased NO_x at the low stoichiometric ratios.

The only second stage variable significantly affecting the minimum NO_x emission was the stage air injector design. Here, it was found that leakage of stage air back into the first stage increased NO_x over the levels attained with complete separation. These results suggest that the dramatic NO_x reduction achieved with the facility are in large part due to the isolation of the stage air from the first stage. The second stage residence time had little effect on NO_x, but did affect CO emissions. Operation at a residence time of 1.0 second or larger and rapid mixing of stage air with the combustion products generally yielded CO emissions of 100 ppm or lower.

A possible design for a 500 MW boiler is presented which shows that utilizing a long first stage residence time under fuel rich conditions increases the boiler size by only 5 percent. Of course, the practical application of this design is dependent upon the availability of cost effective materials for the fuel-rich first stage.

SECTION 1

INTRODUCTION

Utility and industrial boilers are the two largest stationary emitters of NO_x. Together they comprise about 65 percent of nationwide stationary NO_x emissions for the year 1974 (1). Because of this, control of NO_x from utility and industrial boilers has been given high priority in the Federal, state and local NO_x abatement programs to attain and maintain the National Ambient Air Quality Standard for NO_2 (100 mg/m^3). Standards of performance for New Stationary Sources were set in 1971 for gas, oil and bituminous coal-fired steam generators with a heat input greater than 250 MM Btu/hr^2. The standard for bituminous coal units (0.7 lb $NO_2/10^6$ Btu, ~580 ppm at zero percent O_2) is being revised to 0.6 lb $NO_2/10^6$ Btu, ~500 ppm, to reflect advances in control technology (3). The same standard has been recommended for lignite-fired units (4). Standards for new industrial boilers are in preparation by EPA's Office of Air Quality Planning and Standards. Additionally, emission standards for new or existing utility and large industrial boilers has been set as part of State Implementation Plans to maintain air quality in NO_2-critical regions (5).

Despite this concerted regulatory activity, a number of air quality planning studies (6-9) have determined that additional stationary source control technology will be needed in the 1980s and 1990s to meet projected NO_2 air quality needs. These studies have also concluded that, where possible, the additional technology should focus on application to advanced design of new equipment. In response to the need for additional technology, the EPA is developing and demonstrating advanced controls for utility and industrial boilers and other sources (10, 11). The near term emphasis is on use of major hardware modifications for new or existing sources. The far-term emphasis is on major redesign of new sources. The ppm emission goals (at zero percent O_2)

for the near and far term R&D programs for coal-fired utility and industrial boilers are as follows (10, 11):

	1980 Goal	1985 Goal
Utility	230	115
Industrial	175	115

The R&D program discussed in this paper is a component in the Combustion Research Branch of IERL-RTP's effort to generate advanced NO_x controls for utility and industrial boilers firing conventional and alternate fuels (12). To date, the testing has concentrated on utility boiler configurations. The overall goal of these tests is to identify low NO_x operating conditions for the staged combustion of pulverized coal. The results of the program are intended to support both the near-term and far-term efforts mentioned above. To support the near-term application of major hardware modifications on units of conventional design, the test facility was designed with a fairly realistic modeling of the geometry and aerodynamics of large multiburner boilers. This modeling will aid in translating the present pilot scale results to field demonstration or design of major hardware changes. To support the far term application of control through major redesign of new sources, the facility was designed with the flexibility to give a wide variation of the combustion process modifications important in NO_x control. This flexibility offers the capability of identifying combined low NO_x process modifications which are beyond the range of field units of conventional design but which may relate to advanced design. Although the facility was designed to simulate either the front wall-fired or tangentially-fired configurations, a horizontal extension section allowed additional study of the combustion parameters in an axisymmetric flow configuration.

The combustion process modifications investigated in the current test program are as follows:

- Baseline (uncontrolled) burner aerodynamics and wall cooling
- Primary flame zone stoichiometry (stoichiometric ratio, SR)
- First Stage Mixing

- Method of stage air injection
- First stage residence time
- Second stage residence time
- First stage heat release rate and combustion air preheat

These parameters were investigated for the various configurations with the following test objectives as a guide:

- Verify that baseline NO_x emissions and trends with excess air are representative of full scale equipment
- Identify the best combination of low NO_x combustion conditions for
  - Application to conventional designs ($SR \geq 0.95$)
  - Application to major redesign ($SR < 0.95$)
- Identify second stage residence time requirements to achieve CO and carbon burnout at the low NO_x conditions

SECTION 2

EQUIPMENT DESCRIPTION

The experimental facility shown in Figure 1 and described in detail in detail elsewhere (12, 13) was designed to simulate the aerodynamics of either a front wall-fired or tangentially-fired boiler. The basic firebox is a 39-inch refractory lined cube which exits to a refractory lined heat exchange section. Movable heat exchanger drawers allow the variation of the combustion gas quench rate, the furnace residence time or the combustion volume. The primary emphasis in the design of the hardware was to be able to explore staged combustion for NO_x control. Staging ports are provided in each of the heat exchanger sections allowing a variety of first and second stage residence times to be explored. The furnace exhibits the typical heat release per unit volume of coal-fired furnaces at about 1.0 x 10^6 Btu/hr to 1.5 x 10^6 Btu/hr. This firing rate is distributed between five variable swirl burners for the front wall-fired configuration and four corner burners for the tangential configuration. A coal spreader was used to produce the well mixed bulbous flame in the front wall-fired burners and an open tube was used for the delayed mixed axial flames.

Additional hardware utilized for generating some of the data in this paper included horizontal extension sections. These sections, 33-inch inside diameter, shown in Figure 2, allowed for axisymmetric flow and staging at residence times shorter than those feasible with the firebox configuration. Four of the research swirl block front wall-fired burners were used in this configuration at the same combustion intensity as in the firebox configuration. A 16-inch diameter movable refractory choke was used to achieve stage separation when staging.

The various stage air locations referred to in the following text for the firebox configuration are shown in Figure 3.

SECTION 3

EXPERIMENTAL RESULTS

The combustion process modifications investigated in the current test program are as follows:

- Baseline (uncontrolled) burner aerodynamics and wall cooling
- Primary flame zone stoichiometry
- First stage mixing
- Method of stage air injection
- First stage residence time
- Second stage residence time
- First stage heat release rate and combustion air preheat

These parameters were investigated for both the front wall-fired and tangentially, corner-fired configurations with three coal types. Emissions of CO and carbon particulate were monitored for all tests so that the impact of combined low NO_x modifications on unit efficiency could be determined.

Some initial results using an axisymmetric tunnel configuration (horizontal extensions) are also presented. The primary objectives of this later series of tests were to further explore the effects of residence time, first and second stage temperature as well as stoichiometry.

Several definitions need to be emphasized before discussing the data. These are:

Primary Air — Air used to convey the coal to the burner, expressed as percent of total at 15-percent excess air

Secondary Air = Air introduced through the burners into the first stage exclusive of the primary air

First Stage Air = Secondary + primary air

Stage Air = Air introduced into the second stage

Total Air = Primary + secondary stage air

$$\text{Stoichiometric Ratio} = \frac{\text{First Stage Air}}{\text{Stoichiometric Air}} = \text{SR}$$

Residence Time = Mean volumetric residence time of the mass flow using a measured temperature to calculate an average density

3.1 BASELINE CONDITIONS

Since NO_x emissions from coal combustion are highly sensitive to the combustion conditions, the relevance to practical equipment of the low NO_x conditions identified in this facility is reinforced by establishing that the pilot scale baseline emissions simulate results of field tests on full scale equipment.

The first objectives of the present test series were, therefore, to establish a baseline operation representative of full scale equipment. The baseline series of tests consisted of varying the burner settings and the degree of wall cooling to identify the conditions which best represented baseline emission levels and trends with excess air. The base conditions should also correspond to conventional utility practice for fuel/air velocities, primary stoichiometry, air preheat, etc.

Baseline NO emissions were determined for the five front wall-fired IFRF burners using the B&W type coal spreader and for the four tangentially-fired burners. The results are compared in Figure 4 with the pilot scale tests of Armento (14), McCann (15), and Pershing (16) and with the full scale tests of Crawford (17) and Selker (18). Both the front wall-fired and the tangential emissions data compare quite well in overall level and trend with the respective field data. The tangential plot also shows the baseline data for the axial injector in the five front wall burners. Although the axial emissions fall slightly below the resluts with the tangential burner, they are within the range of tangential field data.

The baseline tests discussed above were taken with refractory walls with only natural conductive losses. A number of tests were performed with additional wall cooling but the emissions did not change more than about 7 percent with 300,000 Btu/hr of additional cooling. These results agree with those of other investigators (19, 20, 21). They also found that temperature has little direct effect on fuel N conversion, which accounts for about 80 percent of the total NO_x from coal combustion (19, 20, 22).

3.2 STOICHIOMETRY

NO_x control by staged air combustion has been widely tested since its initial development in the late 1950's (23). Operation with a near or substoichiometric first stage effectively suppresses both thermal and fuel NO_x formation. The degree of NO_x control achieved by increasing fuel-rich stoichiometry may be limited, however, by both practical and theoretical considerations. First, from a practical standpoint there is concern that operations of conventional design boilers at a first stage stoichiometric ratio (SR) below about 0.95 may yield unacceptable rates of water wall corrosion. One objective of the present program was therefore to identify low NO_x conditions for SR $\geq$ 0.95 for potential application to conventional design boilers. Lower SR may be acceptable for new unit redesign, however, so a second objective was to identify the minimum achievable NO_x emission at low SR. Here, fundamental considerations suggest a limit to NO_x reductions. Numerous studies have shown that reduced first stage SR reduces the conversion of fuel N to NO. However, part of the fuel N remains in an intermediary form, primarily HCN, which largely oxidizes to NO in the second stage (24, 25, 26). Additionally, under fuel-rich conditions, hydrocarbon combustion, even in the absence of fuel N, yields bound intermediaries from molecular nitrogen (24, 27, 28).

Staging tests were performed with the stage air introduced into a number of positions in the heat exchange tower while varying the first stage stoichiometric ratio. NO versus the first stage stoichiometric ratio (SR) is shown for both the front wall-fired and tangential configuration in Figure 5 for the second staging position (see Figure 3). The effects of the staging position, i.e., first stage residence time will be discussed later. As seen from the curve, NO is a strong function of the first stage stoichiometric ratio. For the front wall-fired configuration, a 52-percent reduction in NO was achieved at a stoichiometric first stage and an overall excess air of 15 percent. A minimum NO level of 160 ppm was achieved (82-percent reduction) at an SR of 0.80 to 0.85.

For the tangential case, a 31-percent reduction was achieved at a stoichiometric first stage and a minimum of 125 ppm (71-percent reduction) at an SR of 0.85. Further reductions in SR showed a corresponding rise in NO for both configurations at this staging position. Similar results were obtained for the horizontal extension configuration

The speculation is that above an SR of about 0.85, the majority, if not all, NO is generated in the first stage. Below an SR of 0.85, NO very likely decreases in the first stage with decreasing SR. Armento (14) suggests that first stage NO decreases to zero at a first stage equivalence ratio of about 0.65. Figure 5 then suggests that an increasing amount of second stage NO is formed as the SR decreases. This increase also corresponds to an increased heat release in the second stage.

These results are at least in qualitative agreement with equilibrium constraints. For example, Sarofim (Reference 26) has shown that the equilibrium concentration of the bound nitrogen intermediaries in fuel-rich combustion reaches a minimum at an SR dependent on temperature and fuel and increases as the SR is further reduced. Although the equilibrium concentration is low (<100 ppm) at normal coal combustion temperatures, the oxidation of these intermediaries in the second stage can constitute a lower limit to NO_x reduction achievable by staging. Another limiting condition could arise from the fraction of the fuel nitrogen which remains in the coal char after pyrolysis (16, 26). Pershing (16) has estimated that 100 to 200 ppm of total NO_x emissions are due to char NO_x under fuel-lean conditions. Furthermore, the oxidation of the char nitrogen to char NO_x proceeds slowly and is relatively insensitive to first stage conditions. The formation of char NO_x in the second stage could thus limit the effectiveness of staged combustion for NO_x control.

The difference in the minimum achieved between the two firing configurations is believed to be attributable to bulk residence time effects as opposed to localized burner mixing. This will be further discussed in the sections on mixing and residence time. Tests were also conducted to determine the effects of second stage stoichiometry on the overall NO levels. Figure 6 shows several typical curves of NO versus overall excess air at various stoichiometric ratios. As seen here, the overall NO does not seem to be a strong function of excess air under staged conditions. Similar results were obtained for the front wall-fired configuration, for other loads, coals, and staging positions. The only significant effect is noted at SR = 0.65 between 15 and 5 percent excess air. At this SR, the NO decreased by 50 ppm at the lower excess air level. Excess air had a significant effect on CO and carbon loss if the second stage residence time was less than 1 second. In this case, 20- to 25-percent excess air was required to achieve CO levels below 100 ppm at SRs below 0.95. However, when the second stage residence time was at least 1 second, the CO was always under 100 ppm and carbon loss was less than 0.5 percent of fuel input on a Btu basis.

It has been shown NO levels as low as 125 ppm can be achieved with the first stage stoichiometry between an SR = 0.75 to 0.85 and an overall excess air of at least 15 percent to achieve CO and carbon burnout. No significant effect of excess air was seen on NO emissions for most first stage stoichiometries.

3.3 FIRST STAGE MIXING

NO_x emissions from unstaged combustion and from staged combustion at near stoichiometric F/A ratios and above are dominated by burner mixing (17, 19, 22, 29). Detailed study of NO_x control by burner modification is beyond the scope of this program and is covered elsewhere (30). However, the combined effect of mixing and staging was carried through the tests for two reasons. First, burner mixing is important in staging of boilers of conventional design where operation at SR < 0.95 is precluded by operational problems (17, 18). Thus the study of low NO_x conditions for application to conventional designs considered both the front wall-fired and corner-fired configuration with conventional burner designs. Additionally, front wall tests were run with a delayed mix axial injection to bracket effects of high and low rate of mixing with staging. Second, fundamental considerations indicate that burner mixing may be less significant at the low SR potentially achievable with major redesign. As noted above, it is suspected that NO_x emissions at low SR are limited by the chemistry of bound N intermediaries and by the oxidation of char N. From available data and calculations, it is conceivable that under fuel-rich conditions, these limits are controlled more by the overall kinetic and equilibrium condition (bulk temperature, residence time, fuel composition, stoichiometry) than by the microscopic mixing.

The effect of delayed mixed flames under baseline conditions is evident by comparing the results of the spreader nozzle to the results of the axial nozzle as seen in Figure 4. As expected a rather dramatic effect is seen under baseline conditions with the slow mixed flames producing only about 55 percent of the NO of the well-mixed spreader flames.

A comparison of mixing under staged conditions is seen in Figure 7 for the front wall fired spreader and axial configurations at 1.0 and 1.5 x 10^6 Btu/hr load. The influence of first-stage mixing can be seen even under staged conditions where decreased mixing in the first stage produced lower NO for a given stoichiometric ratio, at an SR of 0.85 or greater.

Similarly, the higher load conditions, where more rapid mixing occurs, also produced higher NO than the 1.0 x 10^6 Btu/hr condition over the entire stoichiometric ratio range. However, both temperature and mixing contribute to this increased NO. Again, it should be noted that the role of first-stage mixing decreases as the stoichiometric ratio decreases. It appears that below an SR = 0.75 (0.85 for 1.0 x 10^6 Btu/hr) first stage mixing ceases to have any influence.

3.4 STAGE AIR MIXING

Nearly all prior studies of staged combustion have injected the stage air so that a portion backmixes with the fuel-rich first stage. This backmixing makes it difficult to determine the independent effects on NO_x of first stage stoichiometry, residence time and local fuel/air mixing. Limited results have shown that directing stage air away from the primary flame zone has a substantial effect on NO_x reduction (15, 18). The present facility was therefore designed to achieve a minimum of backmixing into the first stage. The stage air mixing technique was qualitatively studied using cold flow smoke tests. Little backmixing was observed provided the opposed stage air jet impinged at the center of the duct. If the jets impinged on the opposite wall considerable downmixing was observed. Backmixing may account for some of the differences seen in the shape of the curves of stoichiometry versus NO in Figures 5 and 7 for the two staging positions. However, to further illustrate the effect of stage separation, tests were run with biased burner firing using the same primary flame stoichiometry as the staged tests. Also, the method of staged air injection was perturbed to cause backmixing into the first stage and thereby reveal the consequences of backmixing on NO_x emissions. The stage air injection technique was varied to study the effects of second stage mixing on CO and carbon burnout as well as any effect it may have on potential second stage NO. The results of mixing in the second stage are shown in Figure 11.

Three mixing types were explored, fast, slow and downmixing (backmixing). The fast mixing condition uses the normal four 1-inch diameter ports in which the opposing jets meet at the center of the duct under all conditions. The slow mixing case utilized eight 2-inch diameter ports located in two vacant heat exchanger drawer windows as close to the first staging position as possible. Backmixing was achieved by introducing the stage air from one side only at the first staging position.

Figure 8 shows that at a stoichiometric ratio of 0.85, there was virtually no affect of the 3-second stage mixing conditions. However, at an equivalence ratio of 1.02, the slow mix condition gave consistently higher NO levels with the spread in the data being greater with higher excess air. This result is belived attributable to greater backmixing into the first stage. It can be seen that a similar result was obtained for the purposely backmixed condition. It should also be noted that NO is more sensitive to slight changes in the first stage stoichiometric ratio at a SR = 1.02. The conclusion then is that within the staging techniques and SR's tested, the second-stage mixing technique has very little influence on the NO except as it influences the first stage. This effect can also be seen from the biased-fired data point also shown on Figure 8. This case represents the extreme in backmixing where the lower three burners were operated at a SR = 0.85, with the excess air delivered through the upper burners. An effect of the second-stage mixing technique was noted on CO and carbon loss, with the slower mix conditions producing higher CO and carbon (200 to 500 ppm CO and 1 to 2 percent carbon loss). It is therefore critical that a high degree of stage separation be achieved in order to obtain the lowest possible NO for any first stage stoichiometric ratio.

3.5 COAL COMPOSITION

Three different coals were tested to determine the effect, if any, of coal composition on NO emissions for baseline and staged conditions. Table 1 lists the principal properties, nitrogen content and the rationale behind selection of each of these coals.

Although these are some differences between the three coals, the baseline NO emissions for the three coals are not radically different as seen in Figure 9. Emissions with the Montana coal tend to be slightly higher for both the front wall-fired spreader and the tangential configurations.

The effect of coal composition on NO under staged conditions is shown in Figure 10 for the front wall-fired and tangential configurations. For the tangential configuration the Western Kentucky and Pittsburgh data agree closely. The Montana data is higher at baseline but is lower below SR = 0.90. At the rich condition the NO emissions with the Pittsburgh coal did not increase with decreasing equivalence ratio to the same extent as the Western Kentucky coal. The NO from the Montana coal reaches a lower minimum and does not exhibit as much second-stage NO as the Pittsburgh coal below as SR of 0.85. This suggests that at the low stoichiometric ratios the fuel N intermediary products may be different for the three coals.

The staging data for the front wall fired configuration at 1.0 x 10^6 Btu/hr shows a similar trend to the tangential data. However, for the front wall-fired configuration the NO levels of the Western Kentucky and the Pittsburgh No. 8 coals differed at stoichiometric ratios of 1.0 to 0.85. On the other hand, at a firing rate of 1.5 x 10^6 Btu/hr no appreciable difference was observed between the NO levels of these two coals. It is possible that the difference in the 1.0 x 10^6 Btu/hr data was due to changes in mixing patterns caused by buildup of a sticky ash deposit on the fuel tip frequently encountered during the Pittsburgh No. 8 firing. The trend of the NO data for the Montana coal was consistent for all configurations and firing rates. That is, for the Montana coal the NO levels were higher at baseline conditions and SR's greater than 0.80 to 0.85 but achieved a lower minimum at an SR = 0.85.

It appears then that the combustion of Western Kentucky and Pittsburgh No. 8 coals yield quite similar results. The Montana coal acts differently under both baseline and staged conditions. This difference may be attributed to the lack of sulfur and/or water content of this coal.

3.6 LOAD REDUCTION

Under normal operation, reduced load (volumetric heat release rate) and reduced air preheat tend to reduce NO_x emissions by suppressing thermal NO_x. Indeed, new boiler designs are using enlarged fireboxes partly to meet NO_x emissions standards (3). Under fuel-rich conditions, however, opposite effects may prevail. The work of Sarofim, et al. (26, 28, 31) has suggested that high heat release rate and/or high preheat may reduce NO_x in two ways. First, high bulk temperature can accelerate the decay of superequilibrium concentrations of bound N intermediaries in the first stage and thus reduce the conversion to NO in the second stage or accelerate the decay of superequilibrium levels of NO. Second, high first stage temperature can reduce the amount of bound nitrogen carried into the second stage in the char.

First, the effect of load was determined at baseline condition for the front wall and tangentially-fired configurations. This is shown in Figure 11. The trend with excess air is similar for the two configurations but the higher load yields a 25-percent increase for front wall firing and a 40-percent increase for tangential firing. This increase is attributable to both aerodynamic effects and temperature. The high load firing produced more intense sharply defined flames for both tangential and wall firing.

The differences in load under staged conditions are seen in Figure 12. High load firing yielded lower NO_x below SR = 0.75. This result is in line with the mechanisms suggested above. Further evidence for these mechanisms will be covered in the subsection on residence time and preheat.

3.7 FIRST STAGE RESIDENCE TIME

Conventional applications of staged combustion inject the staged air directly over the primary flow with a resulting first stage residence time of less than 1 second. This is done both for convenience and to ensure adequate second stage residence time for CO and carbon burnout. Several studies have suggested, however, that increased first stage residence time enhances NO_x reduction (15, 18, 25, 32-34). This is consistent with fundamentals since increased residence time at fuel-rich conditions should promote the reducing reactions involving bound nitrogen intermediaries and should also promote the driving off of the char-bound nitrogen prior to oxidation in the second stage. At very rich conditions, however, there could conceivably be compensating effects due to increased formation of bound nitrogen from molecular nitrogen.

Tests were conducted in the front wall-fired configuration, the tangentially-fired configuration and the horizontal extension mode to explore the effects of residence time. With the main firebox, three stage air injection positions (see Figure 3 for location) and two loads, 1.0 and 1.5 x 10^6 Btu/hr, were investigated. With the horizontal extension configuration (Figure 2) much shorter residence times were explored at loads of .85 and 1.3 x 10^6 Btu/hr. The reduced loads were used in order to maintain approximately the same heat release per unit volume as with the firebox configuration. Also four burners were used instead of five in order to maintain constant burner aerodynamics. Baseline tests in this horizontal extension mode revealed near identical NO versus excess air curves as compared to the front wall-fired firebox data.

The variation of NO with residence time* is shown in Figures 13 and 14 at various first-stage stoichiometric ratios for the front wall and tangentially-fired configurations, respectively. The variation in NO with residence time for the horizontal extension over a much broader range of residence times is shown in Figure 15.

This data leads to the following conclusions:

- At 1.65 $\geq$ SR $\geq$ 0.95 NO decreases with increasing residence time with the rate of decreasing leveling off after 3 to 3.5 seconds
- To achieve a lower overall NO value for a given residence time the stoichiometric ratio must be lowered. However at low SR's and at

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*The residence times here are volumetric bulk residence times determined by the mass flowrate and flue gas density calculated at an average temperature of 2,200°F assuming a well stirred reaction over the furnace volume. It should be remembered that the first stage residence time at a SR = 0.75 will be considerably longer for a given configuration than at the baseline stoichiometry with 15- to 30-percent excess air as experienced in conventional boilers.

the longer residence times, it appears that sufficient intermediary species are formed and then converted to NO in the second stage to cause the overall NO to increase again.

- In the firebox configuration and at a low stoichiometric ratio an increase in combustion intensity could be traded for longer residence times. However, this was not clearly demonstrated in the horizontal extension configuration.
- Taking all the data into consideration and using the staging techniques employed here, it does not appear that NO levels below 100 ppm can be achieved just be extending the residence time alone
- The lower NO exhibited by tangential firing at low stoichiometries may be due to a longer bulk residence time compared to wall firing. If the tangential data at SR = 0.85 were shifted by an increase in residence time of 0.9 seconds, the tangential and front wall-fired data would coincide. The rationale behind this is that the burner is located physically lower in the firebox and the tangential rotation may result in an effective longer residence time.

To gain additional insight into the formation and decay of NO in the first stage, sampling in the hot fuel-rich first stage in the horizontal extension configurations was performed using the probe shown in Figure 16. This is a water cooled, water injection probe which rapidly quenches the hot gases and coal or char particles sampled from the first stage. The horizontal extensions were set up with the stage air introduced at the longest possible residence time and with samples taken at various distances (or residence times) from the burner. Figure 17 shows the NO levels as a function of residence time and stoichiometric ratio. These data show that the NO levels reach a peak early in the first stage and then decay with increasing residence time. At sufficiently low SR ($\leq$0.65) the NO appears to nearly vanish; thus adding further evidence that particularly for the long residence time configurations, second stage NO is probably being formed from the intermediary XN species. These data also show that the peak is dependent on the stoichiometric ratio. Sampling for other XN species is needed to determine if the fuel nitrogen is being converted to N_2 or other XN's, which are eventually converted to NO in the second stage.

3.8 SECOND STAGE RESIDENCE TIME

The effect of second stage residence time was explored by keeping the stage air location constant and moving the heat exchange surface. Figure 18 shows the effect of second stage residence time as a function of stoichiometric ratio and second stage mixing technique. As can be seen, no effect was observed indicating that for these equivalence ratios second stage NO is being formed very rapidly.

However, one practical limitation to staged combustion has been the occurence of CO and carbon-in-flyash emissions at low stoichiometric and/or low second stage residence times (15, 18, 32-34). One objective of the present program associated with the identification of the best combined low NO_x operating condition was the identification of the second stage residence time required for CO and carbon burnout. This requirement impacts the feasibility of the present results for application to both conventional designs and advanced designs. It was found that with 15 percent excess air and a second stage residence time of 1 second or longer, CO levels were below 100 ppm and carbon losses were below 0.5 percent of the heat input. The minimum second stage residence time was reduced at high levels of excess air.

3.9 TEMPERATURE

As mentioned in the section on load reductions, theoretical considerations indicate that higher temperature or load may drive the NO and XN reducing reactions at a faster rate if a superequilibrium condition exists in a fuel-rich environment. Therefore, it would be expected that under fuel-rich conditions increased air preheat would also lower the NO levels. Under the fuel-lean environment, the NO emissions should be higher for the higher preheat. Indeed the data (Figure 19) reflects these trends although the effect is not strong for the fuel-rich condition. The higher NO emissions for SR's ≥ 0.90 are attributed both to a higher thermal portion and to a significant change in the aerodynamics as the burner exit velocities change with preheat. That is, for the cold conditions, the flame begins to resemble a delayed mixed flame.

Figures 12 and 19 show that for reducing conditions increased preheat and or load is marginally desirable. However, there may be a limit to this temperature effect. That is, it is also possible that if the temperatures are sufficiently high (near adiabatic) the equilibrium levels will increase as shown by Sarofim in Figure 20, such that the driving function for the decay reaction is less or even in the wrong direction. Thus, if the gas temperatures are near adiabatic conditions, the NO levels may be subequilibrium resulting in higher NO with additional preheat. Thus, although some preheat may be desirable, very high temperature conditions could be undesirable.

3.10 SUMMARY

A summary of the major findings of this work is presented by major test parameters in Table II. The results are categorized into low and medium stoichiometric first stage. An indication is given for each test parameter whether it has a major, moderate or minor effect on NO and the preferred value or direction for that parameter. A brief reiteration of the findings are discussed below for each test parameter:

- Stoichiometry — First stage

  NO is a strong function of stoichiometry with a minimum occuring at an SR of 0.75 to 0.85. This minimum SR is also a function of residence time with the minimum SR point decreasing with decreasing residence time.

- Excess air

  Following the fuel rich regime, the amount of excess air does not affect the NO levels except at SRs below 0.75. This implies second stage NO is formed very rapidly with a minimum of excess air. Excess air does affect CO and carbon burnout. A minimum of 15 percent is required if the second stage residence time is about 1 second.

- Burner mixing

  The effect of burner mixing under the configurations testud (spreader versus axial nozzle and tangential) showed that burner mixing became less important as the stoichiometric ratio decreased. Below a stoichiometry of 0.8, no difference in the NO levels was observed.

- Stage separation

  It was observed taht backmixing into the first stage from the second stage increased the NO levels. The method of stage air mixing had no effect on the total NO levels unless it influenced the first stage stoichiometry. Good stage separation is recommended.

- First stage residence time

  Hot sampling and residence time studies revealed that the NO levels reach a peak early in the flame history and decay with residence time under fuel-rich conditions. The peak is dependent on the stoichiometric ratio of the first stage and the decay rate may be proportional to the temperature level. Using conventional staging technology, it takes 3 to 3.5 seconds to get to 100 ppm at a stoichiometric ratio of 0.75 to 0.85. Lower stoichiometric ratios result in the generation of second stage NO, probably from XNs formed in the first stage.

- Combustor air preheat and heat release rate

  It appears that increased temperature in the first stage either by increasing combustion air preheat or heat release rate increases the decay rate of NO in a fuel rich environment. This effect was much more noticeable with increased heat release rate than with air preheat. The higher heat release rate produced similar NO levels but at shorter residence times than the lower heat release rate. Theoretical considerations indicate though that there may be a limit to this effect as the temperatures approach adiabatic levels. At adiabatic conditions, the equilibrium levels, even under fuel rich conditions, are on the order of 1000 ppm.

- Second stage residence time

  No effect of second stage residence time on NO was observed. This evidence together with the lack of effect of excess air (fuel-rich in the first stage) and second stage mixing technique indicated that second stage NO when it is formed (at $SR \geq 0.75$) is formed very rapidly. At least 1 second at 15-percent excess air is needed for CO and carbon burnout.

SECTION 4

DISCUSSION AND PRACTICAL IMPLICATIONS

Perhaps the most significant concept that has come out of this study is that one technique of achieving low NO emission is through an optimum low stoichiometric ratio held for sufficiently long residence times to allow for NO and XN decay. Although it is realized that this concept may not be practical for retrofit of existing boilers, it may be applicable to new boiler design where there is more freedom to consider radical design alternatives.

The principle problem of using this design concept even for new boilers will be in finding materials to withstand the reducing, sulfer-laden high temperature atmosphere. Slagging and corrosion from the ash are also likely to be significant problem areas. Assuming for the moment that these problems can be solved at reasonable cost, the boiler would have the following general specifications:

- First stage stoichiometry of 0.75 to 0.85
- First stage residence time 3 to 3.5 seconds
- Combustion air preheat of 600°F or greater
- If possible, low heat absorption in the first stage
- Separation of the first and second stage through the use of a baffle or overhang
- Rapid mixing of the second stage air, possibly at the baffle
- Second stage residence time of at least 1 second with 15 percent excess air

Figure 21 shows these general specifications applied to the design of a 500 MW boiler in comparison to a conventional boiler. In this design, a first stage bulk residence time of about 3.5 seconds has been assumed at a stoichiometric ratio of 0.75. A second stage residence time of 1.3 second was chosen to the superheater tubes with an overall excess air of 15 percent. This results in an overall height of 131 feet compared to 125 feet for the conventional uncontrolled design where a 14,000 Btu/hr-ft^3 heat release per unit volume was assumed. This advanced design has about a 5 percent increase in side wall area. For a new unit, this increase in area would probably not represent a significant cost increase to the power plant. However, with 2/3 of the boiler operating in a fuel rich environment, expensive exotic materials and more sophisticated control and flame safeguard equipment may be required. This new design should be able to achieve NO emission as low as 100 ppm. Considerably shorter periods in the fuel rich zone would result in slightly higher NO levels and less surface area would be exposed to the fuel rich atmosphere. The desired NO level will, therefore, dictate how much volume will be needed in the fuel rich zone as illustrated in the design curves, Figures 13 to 15 in Section 3.

If a low stoichiometric ratio cannot be achieved, such as in retrofitting an existing boiler, then the design will change slightly.

If a first stage equivalence ratio of 0.95 to 1.0 is selected, the first stage mixing becomes important. It is desirable in this case to select delayed mixed burners which produce an axial flame. Also, under these conditions low preheat or low combustion intensity is desirable as seen in Figure 19 for the tangential configuration. Introduction of the stage air should be delayed again as long as practically possible, while maintaining CO and carbon burnout. That is, the stage air ports should again be as far as possible from the burners. In addition, some mechanism should be employed to prevent backmixing into the first stage whether it be the injection technique or an overhang or baffle. Rapid mixing of the second stage air is desirable to enable burnout of CO and carbon.

In summary, then considerable data have been presented outlining the effects of first and second stage parameters on NO emissions for both front wall-fired and tangential configurations. And it has been shown how these data may be applied to the practical design of a new boiler or to the retrofit of existing hardware.

However, it appears that achieving low NO emission (100 to 200 ppm) in relatively short residence times (1 to 2 seconds) and at stoichiometric ratios ≥0.95 is not feasible with conventional staging technology. It will probably be necessary to combine staging with a delayed mix burner design to achieve these low levels.

In order to gain a better understanding of the formation and fate of NO under staged conditions, additional hot sampling in the fuel-rich first stage is needed. Not only should NO be mapped, but the time history of the intermediary compounds (NH_3, HCN, etc.) should be determined. If it is feasible to obtain this data then it should provide a clearer understanding of the role of each of these compounds and the fate of NO, and may provide some insight into the proper times and methods for fuel air mixing.

In addition to the above, the materials under the reducing conditions in the first stage over long periods of time needs investigation to insure that this staging concept is indeed a viable technology.

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30. Heap, M. P., et al., "The Optimization of Burner Design Parameters to Control NO_x Formation in Pulverized Coal and Heavy Oil Flames," in *Proceedings of the Stationary Source Combustion Symposium, Volume II*, EPA 600/2-76-152b, June 1976.

31. Pohl, J. H. and A. F. Sarofim, "Fate of Coal Nitrogen During Pyrolysis and Oxidation," in *Proceedings of the Stationary Source Combustion Symposium, Volume I*, Fundamental Research, EPA 600/2-76-152a, June 1976.

32. Heap, M. P., et al., "The Control of Pollutant Emissions from Package Boilers," ASME paper 75-WA/Fu-4, December 4, 1975.

33. Siegmund, C. W. and D. W. Turner, "NO_x Emissions from Industrial Boilers: Potential Control Methods," ASME Journal of Engineering for Power, p. 1, January 1974.

34. Cato, G. A., et al., "Field Testing: Application of Combustion Modification to Control Pollutant Emissions from Industrial Boilers – Phase 2," KVB Engineering, Environmental Protection Technology Series, EPA 650/2-76-086a, April 1976.

TABLE I. PULVERIZED COAL COMPOSITIONS

	Pittsburgh #8	Western Kentucky	Montana-Powder River Region
Ultimate Analysis (%, dry)			
C	77.2	73.0	67.2
H	5.2	5.0	4.4
N	1.19	1.40	1.10
S	2.6	3.1	0.9
O	5.9	9.1	18.0
Ash	7.9	8.1	11.3
Heating Value (Btu/lb, wet)	13,730	12,410	8,900
Proximate Analysis (%, wet)			
Volatile	37.2	36.1	30.5
Fixed Carbon	53.0	51.2	39.6
Moisture	1.3	4.8	21.2
Ash	7.1	7.8	8.7
Rationale for Selection	● Most important general class of U.S. steam raising coals ● Highest quality U.S. steam coals ● Standard against which others are usually compared ● Wide distribution ● Expanded production likely	● Extensively used for steam generation in Ohio and Mississippi valley areas ● Good quality steam coal ● Wide distribution ● Some published flue full-scale data for comparison	● Current local importance, future national significance ● "Typical" western subbituminous in abundant supply

TABLE II. SUMMARY OF MAJOR FINDINGS

Test parameter	Baseline and moderate staging (SR ~0.95)	Low stoichiometry (SR ~0.8)
Excess air	Moderate effect; increases NO_x	Minor effect on NO_x; reduces CO and carbon
Burner mixing	Major effect; delayed mix burners preferred with staging	Minor effect
Stage separation	Major effect; low backmix preferred	Major effect; low backmix preferred
First stage residence time	Minor effect at low load; major effect at high load	Moderate effect at low load; major effect at high load
Heat release rate	Moderate effect; increases NO_x by increased temperature, increased mixing	Moderate effect; decreases NO_x at fixed residence time
Combustion air preheat	Minor effect; increases NO_x by increased combustion temperature and changing aerodynamics	Minor effect; decreases NO_x
Second stage residence time	Minor effect on NO_x; CO and carbon burnout achieved	Minor effect on NO_x; CO and carbon burnout achieved

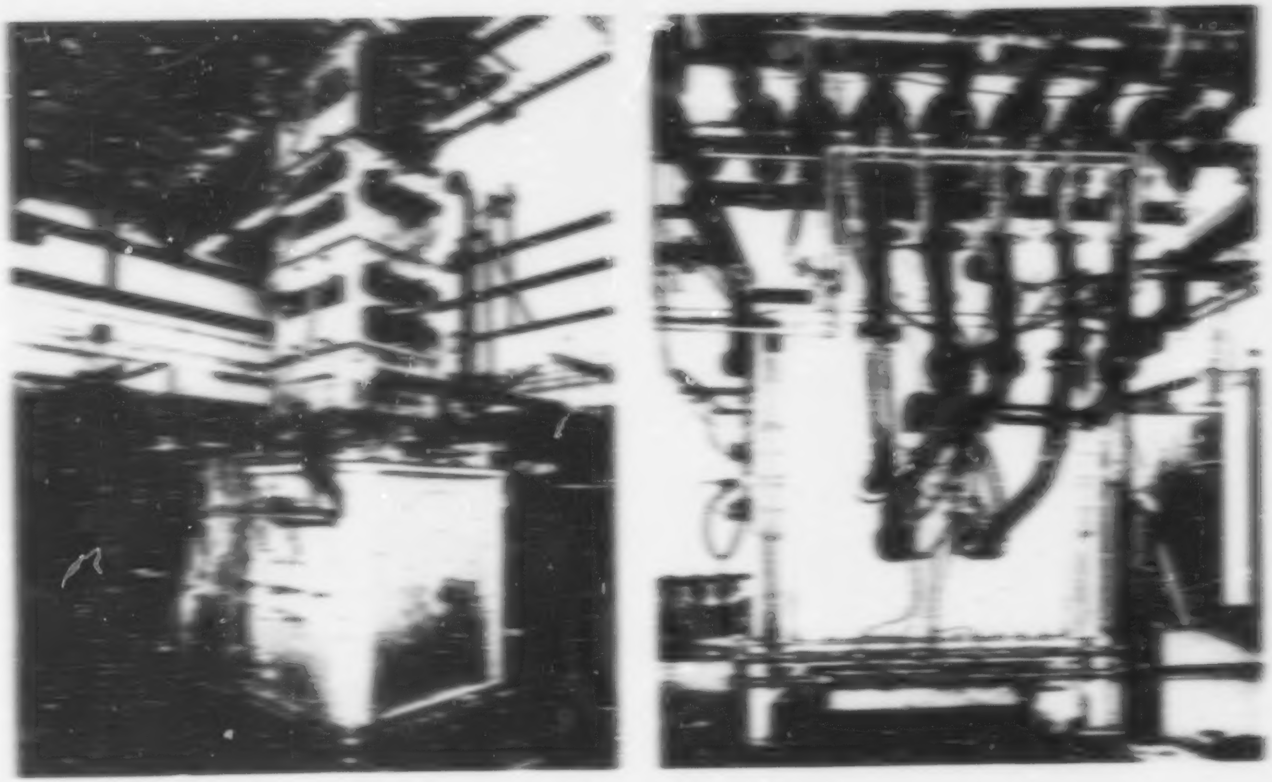


Figure 1. Coal/oil/gas/combustion.

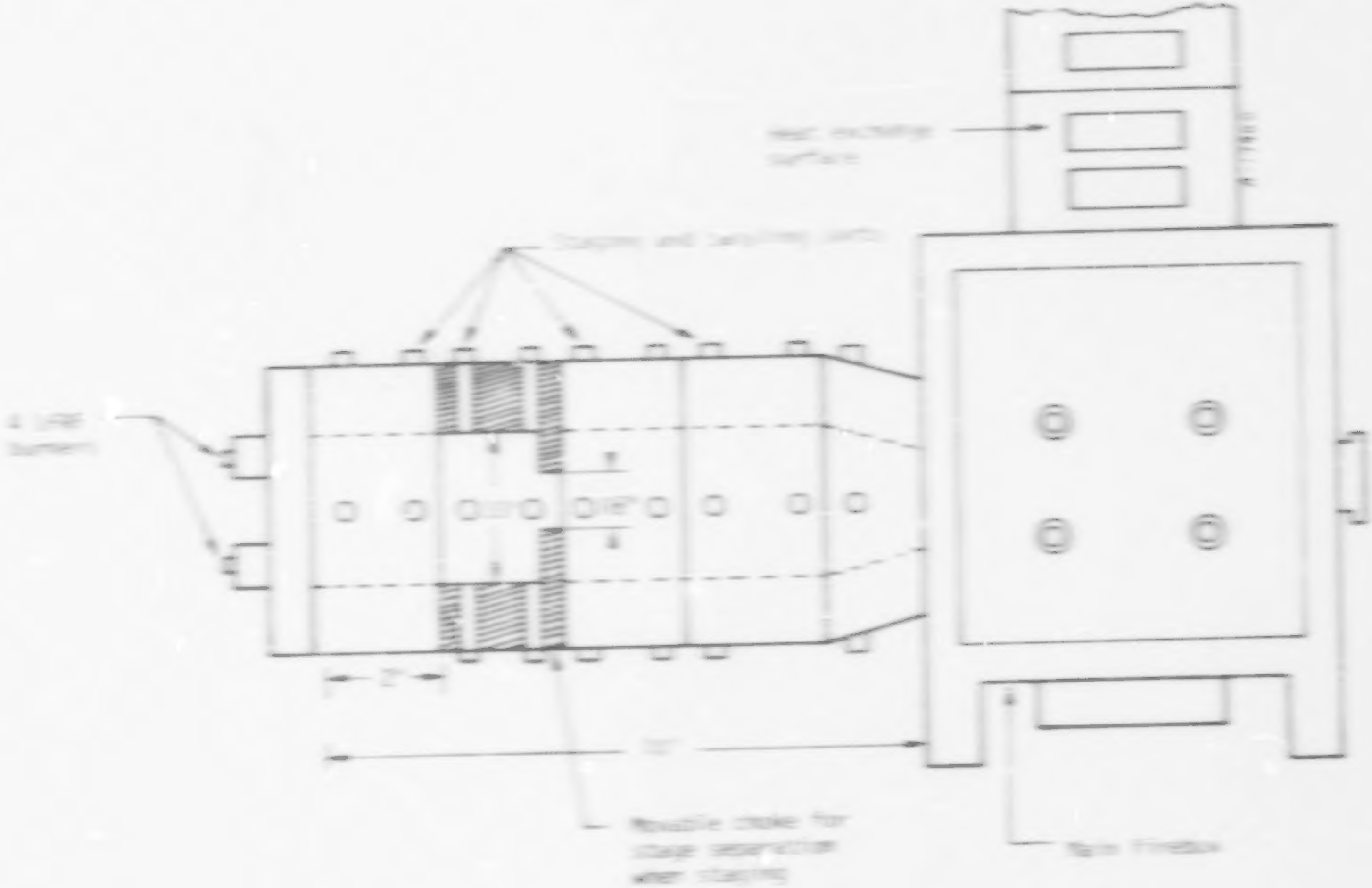

Heat exchange surface
Staging and sampling ports
4 LPAF burners
2"
Movable choke for stage separation when staging
Main firebox

Figure 2. Horizontal exterior configuration.

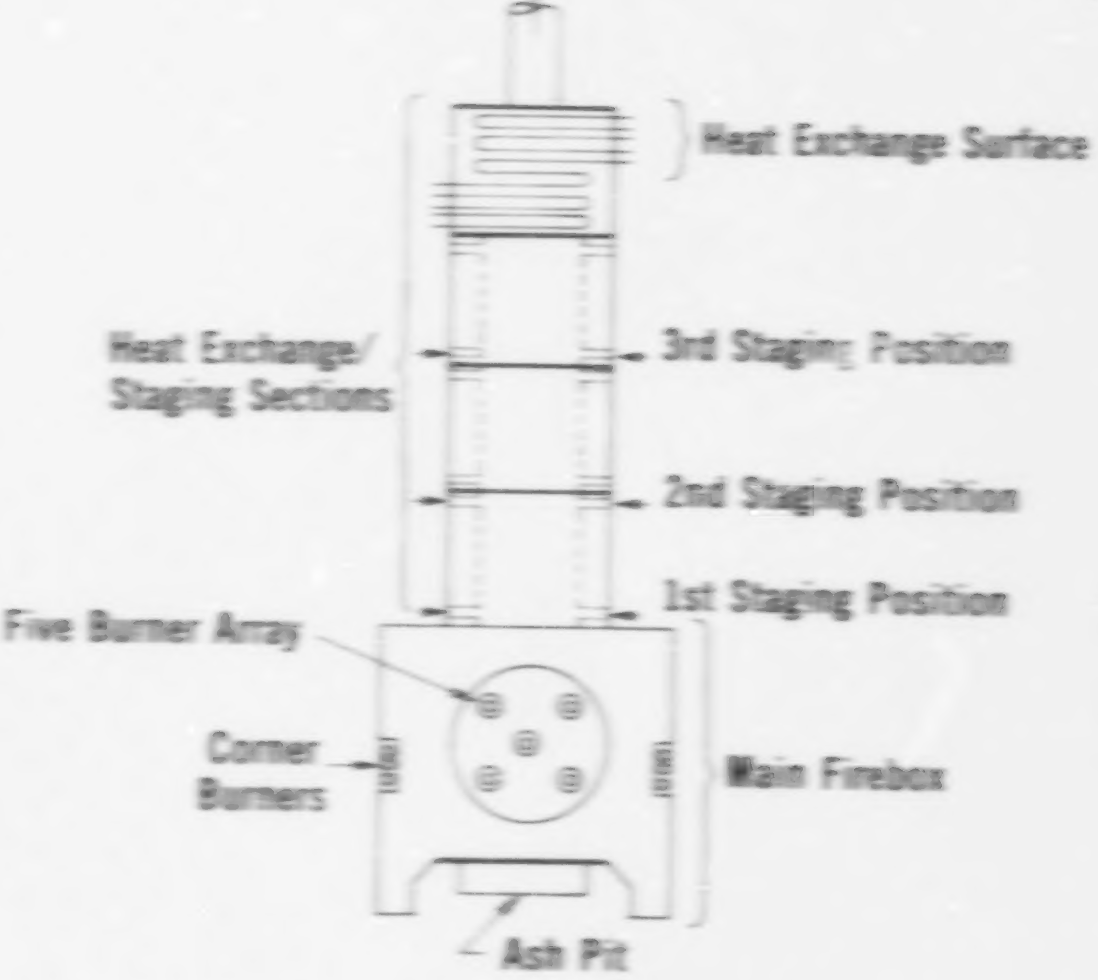
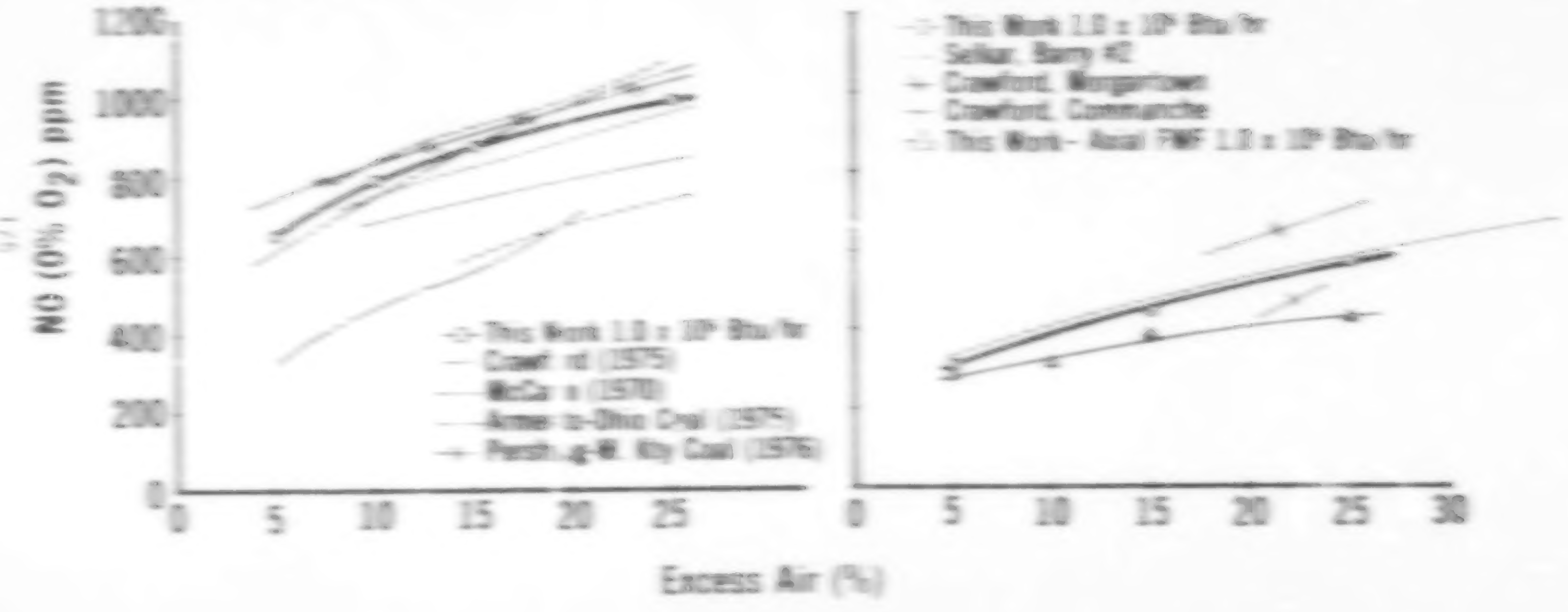

Heat Exchange Surface
Heat Exchange/
Staging Sections
3rd Staging Position
2nd Staging Position
1st Staging Position
Five Burner Array
Corner
Burners
Main Firebox
Ash Pit

Figure 1. Staging air locations.



Base Conditions — This Work
Western Kentucky Coal
Swirl Index = 4
Primary Air = 12%
600°F Preheat
5 IFRF Burners
B&W Type Spreader

Base Condition — This Work
Western Kentucky-Coal
YAW = 6°
Primary Air — 15%
600°F Preheat
4 Tangential Burners

Figure 4. Baseline NO.

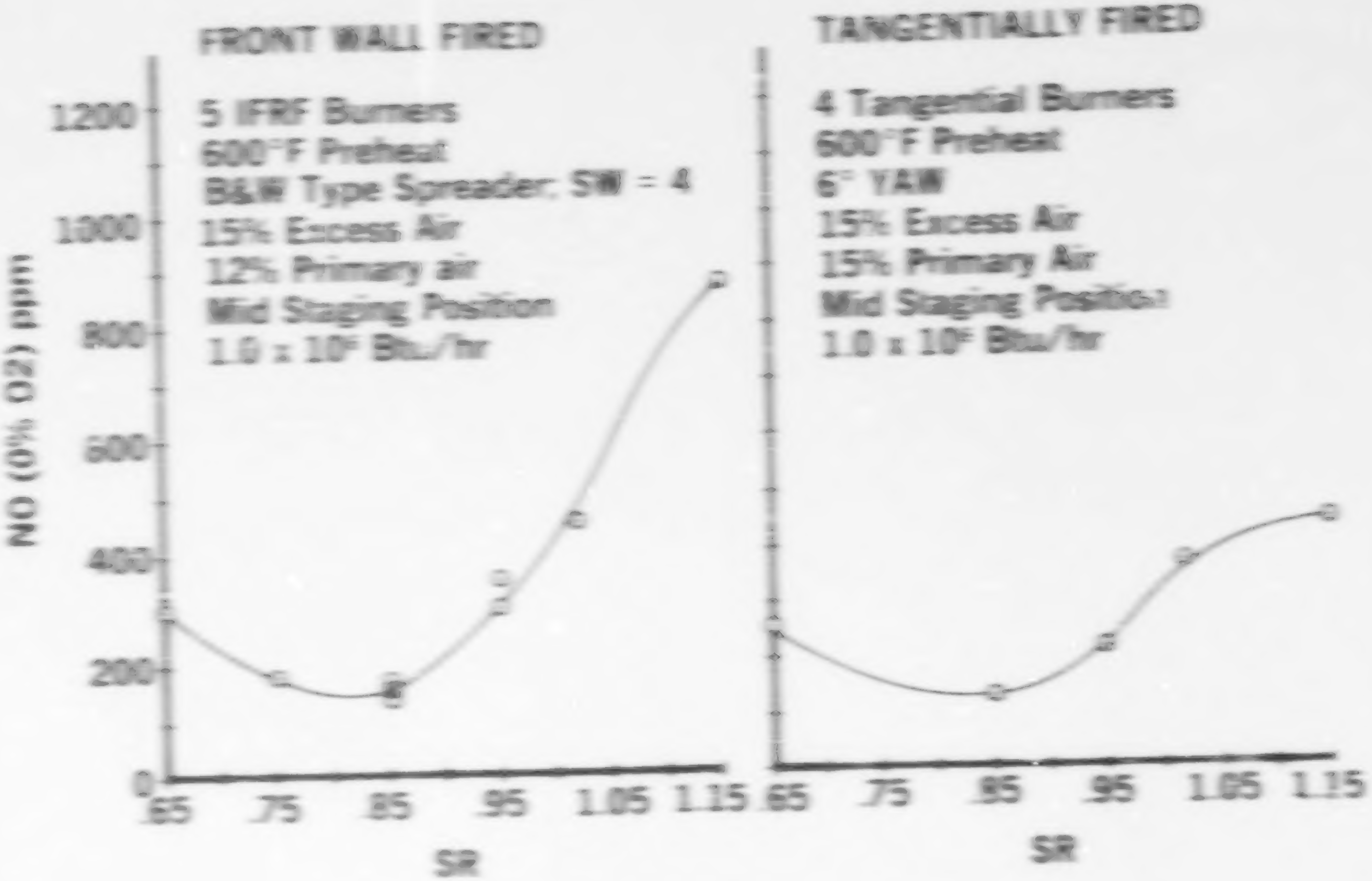


Figure 5. Effect of stoichiometry - first staged.

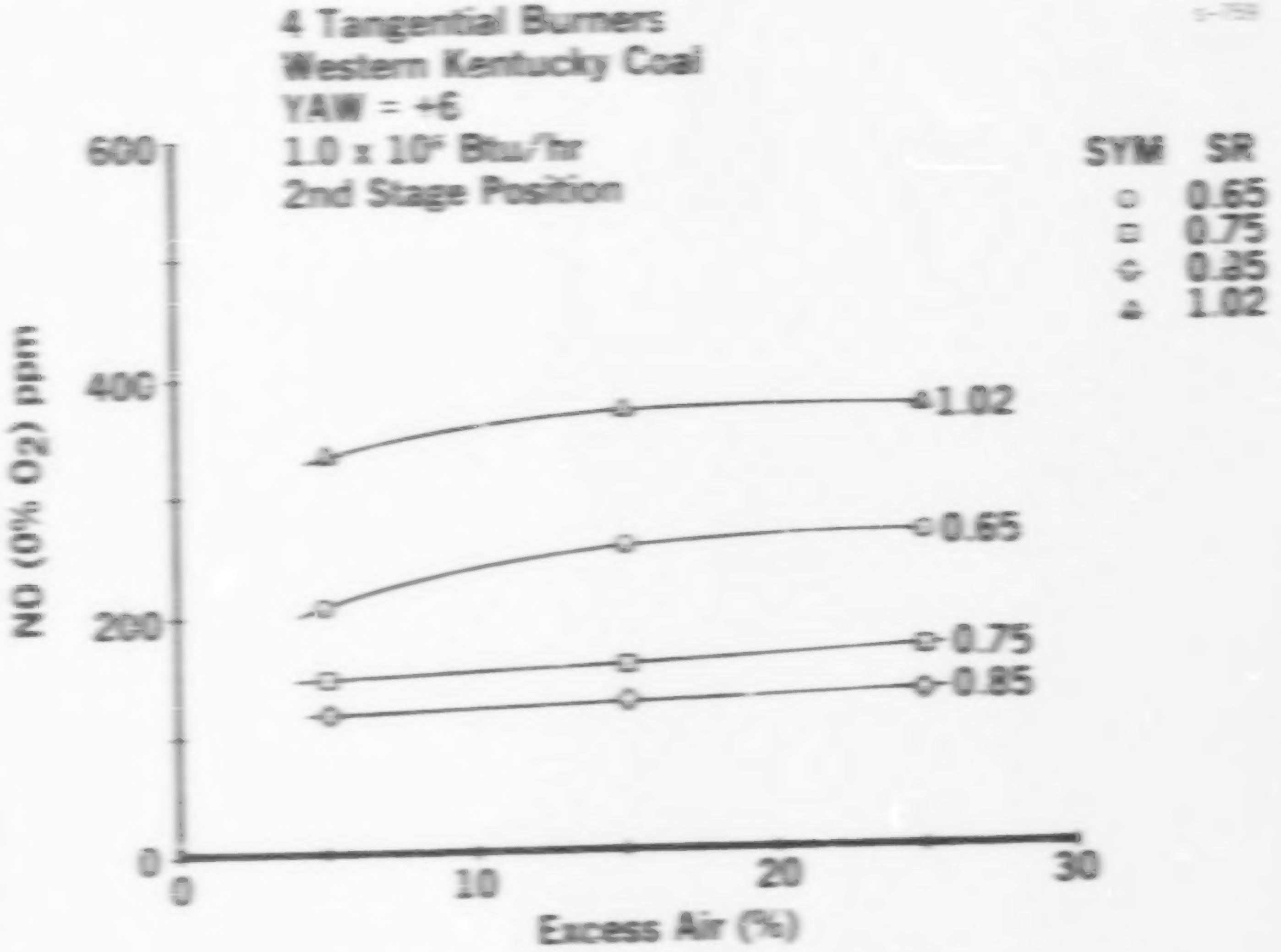


Figure 6. Effect of stoichiometry - second stage.

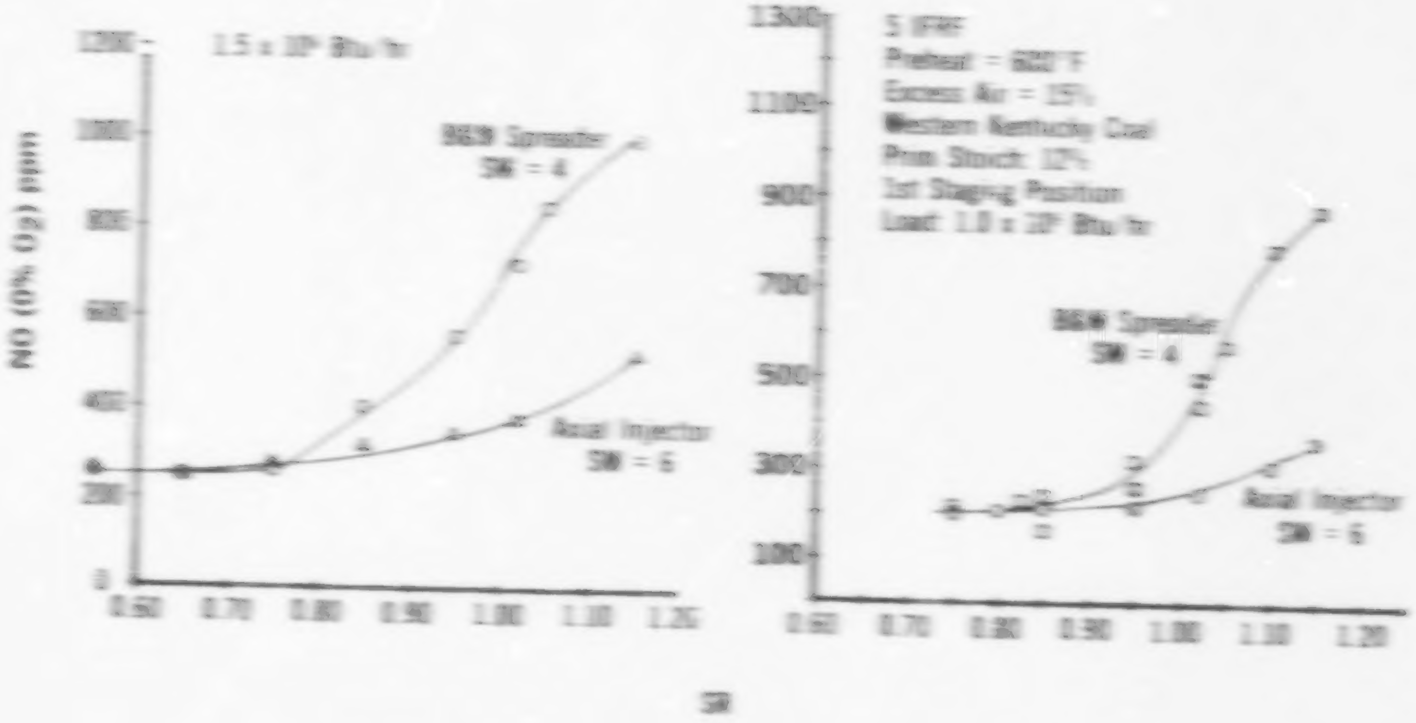


Figure 7. Effect of mixing - first stage.

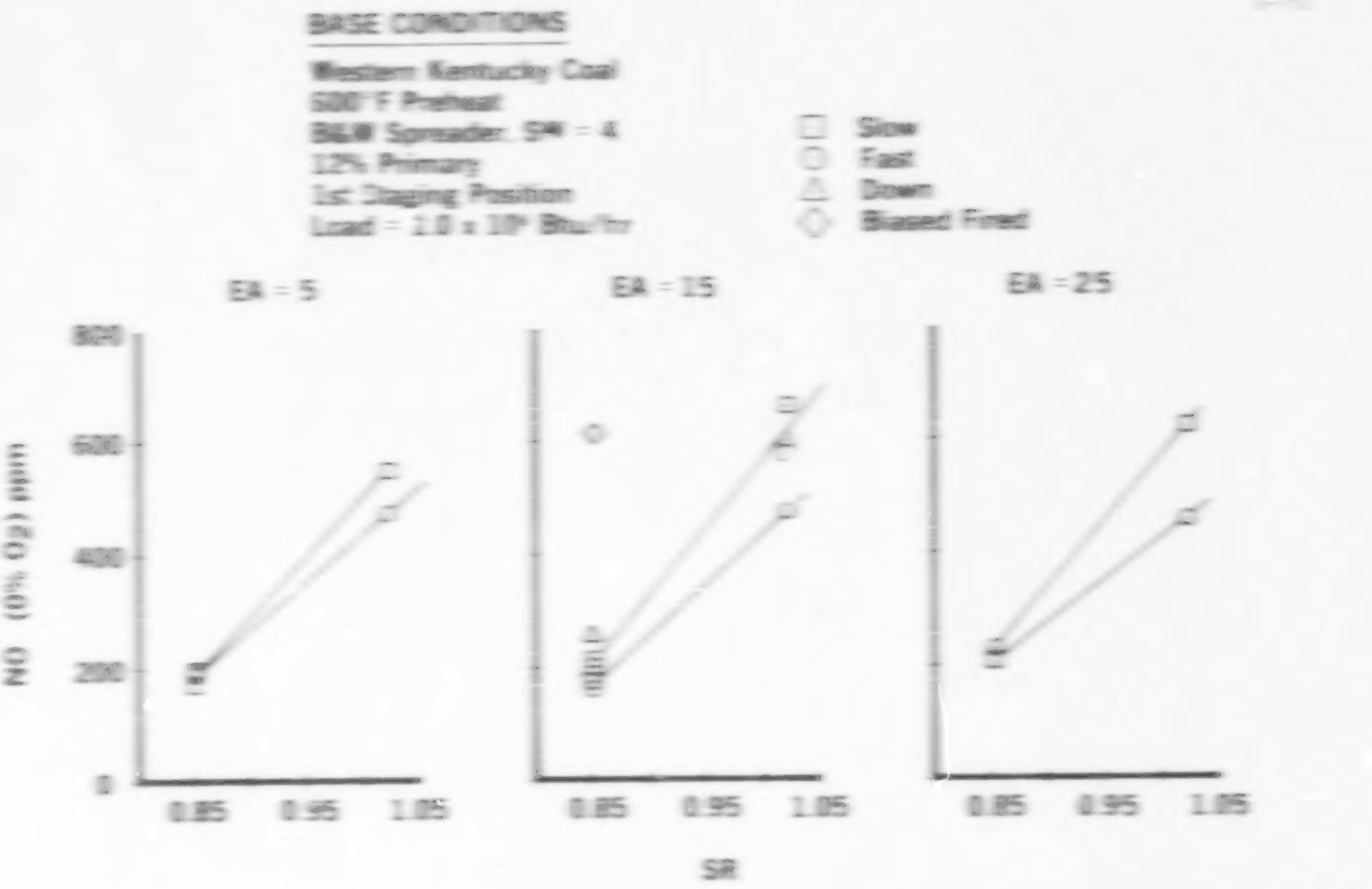


Figure 8. Effect of second stage mixing.

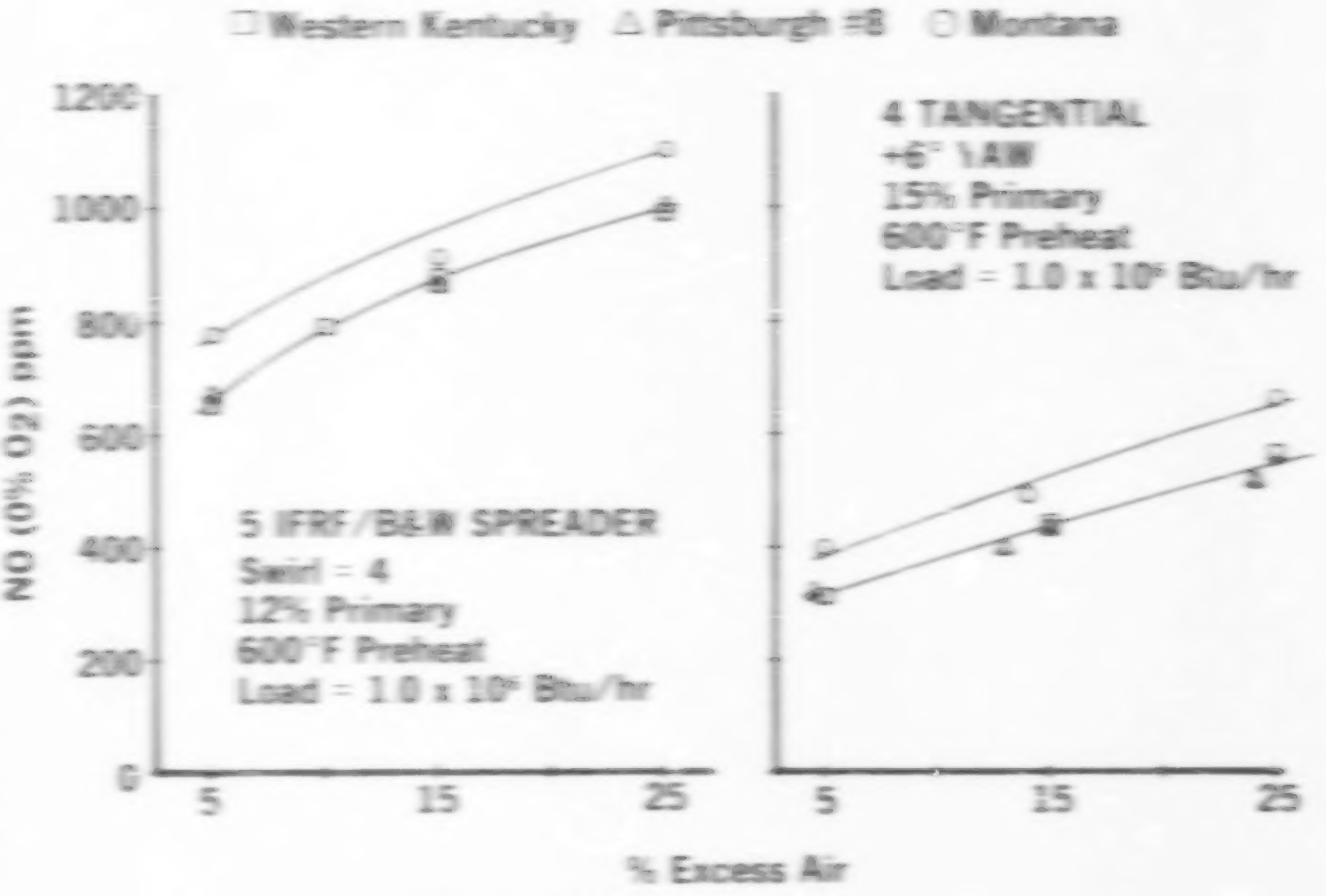


Figure 8. Effect of coal composition - baseline.

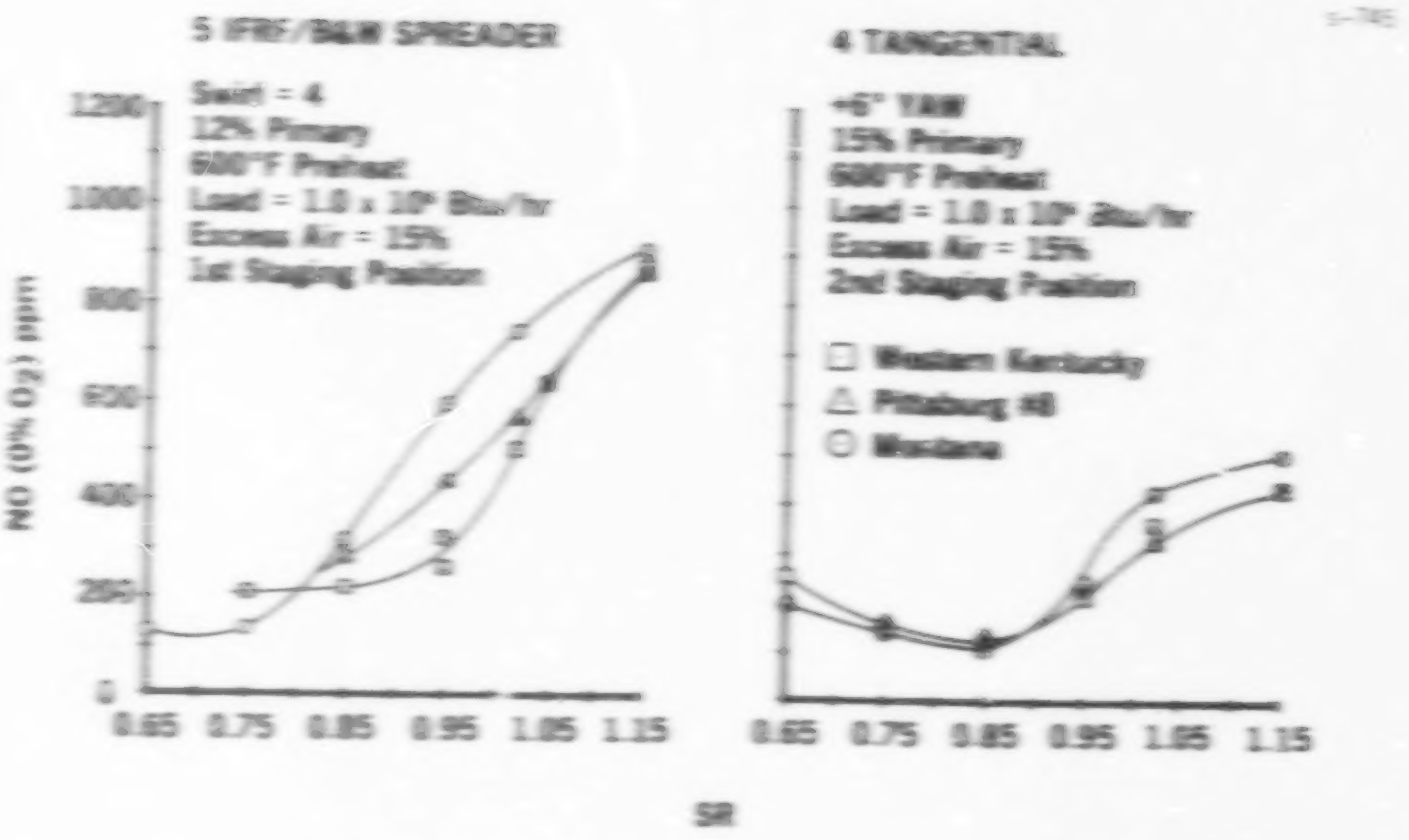


Figure 10. Effect of coal composition – staged.

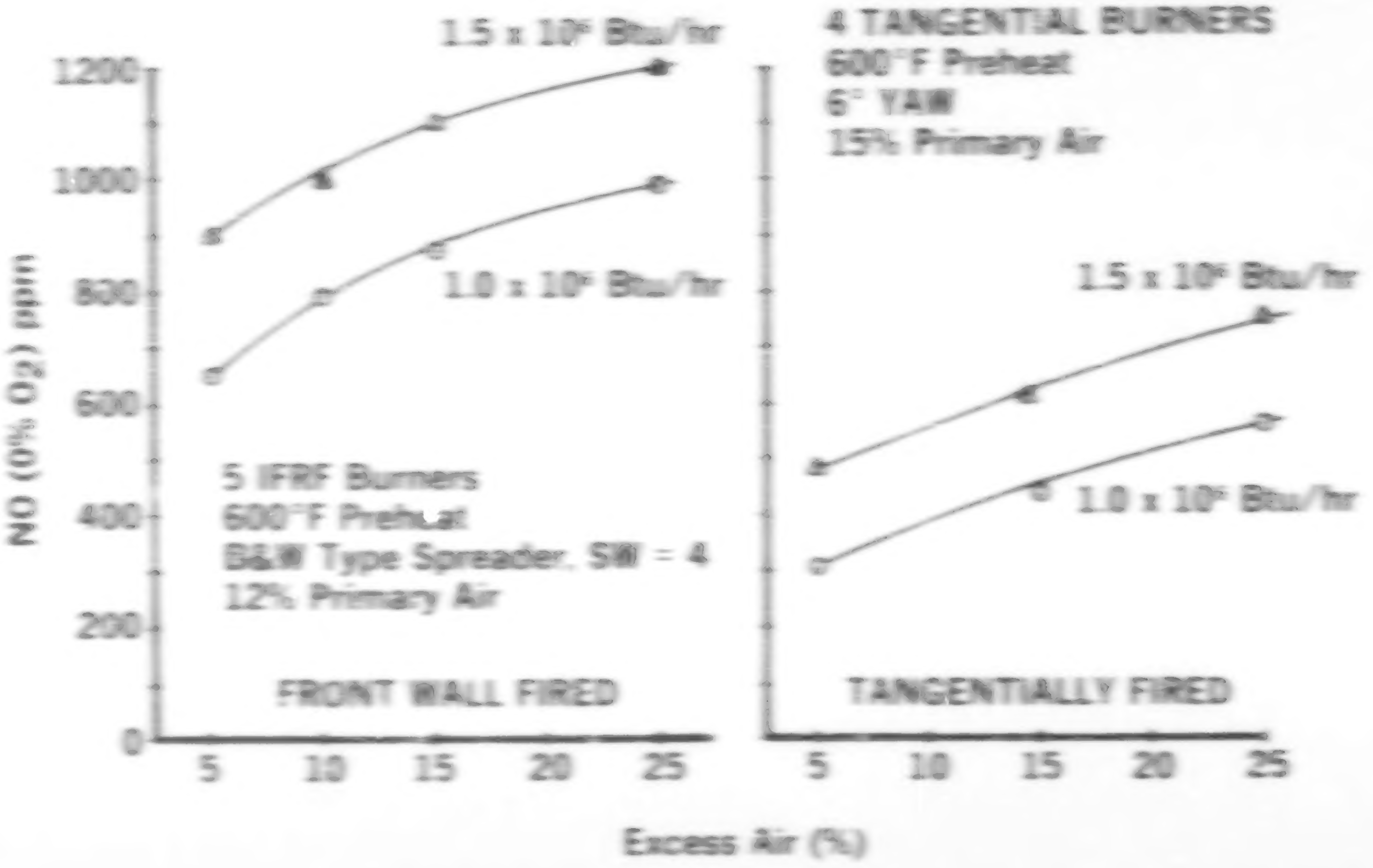


Figure 11. Effect of load - baseline.

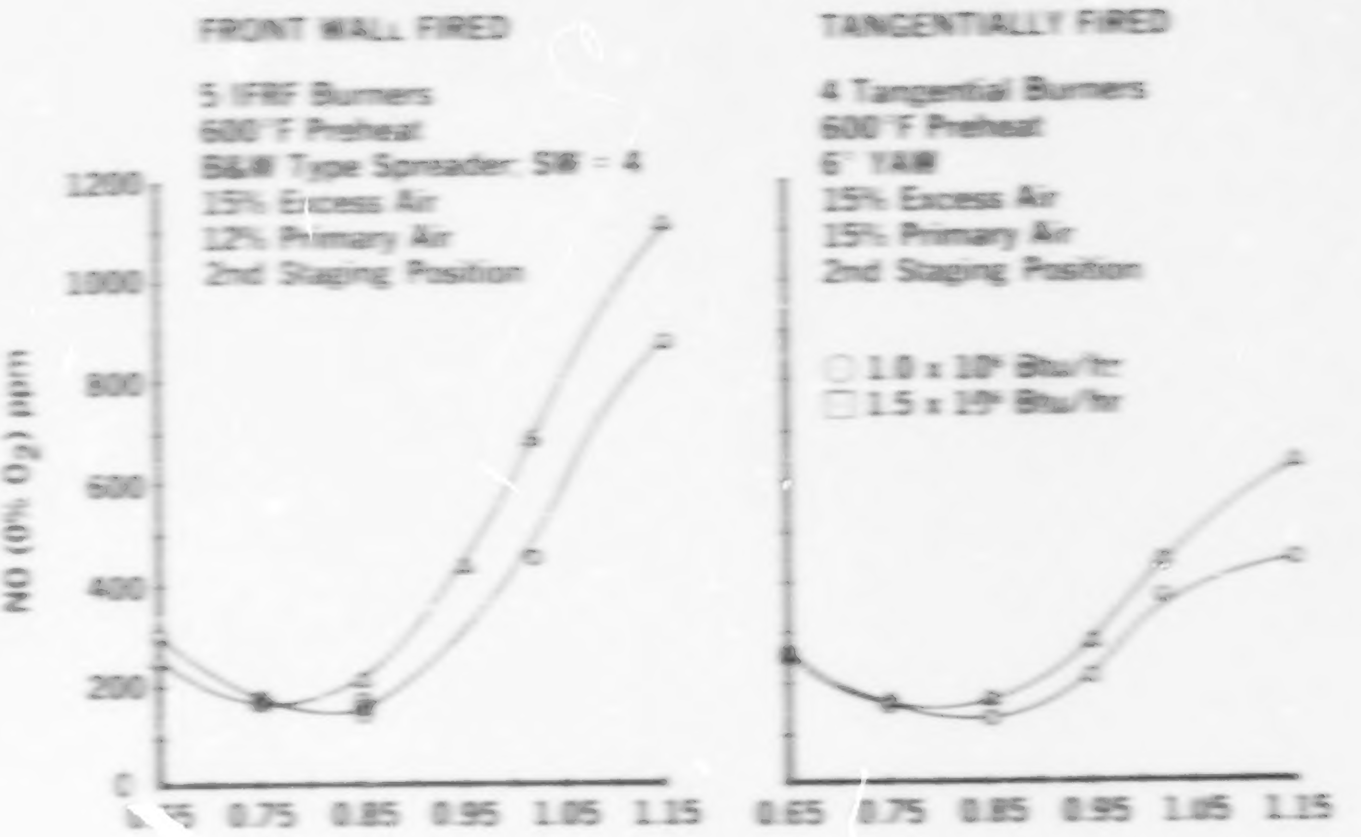


Figure 32. Effect of load - staged.

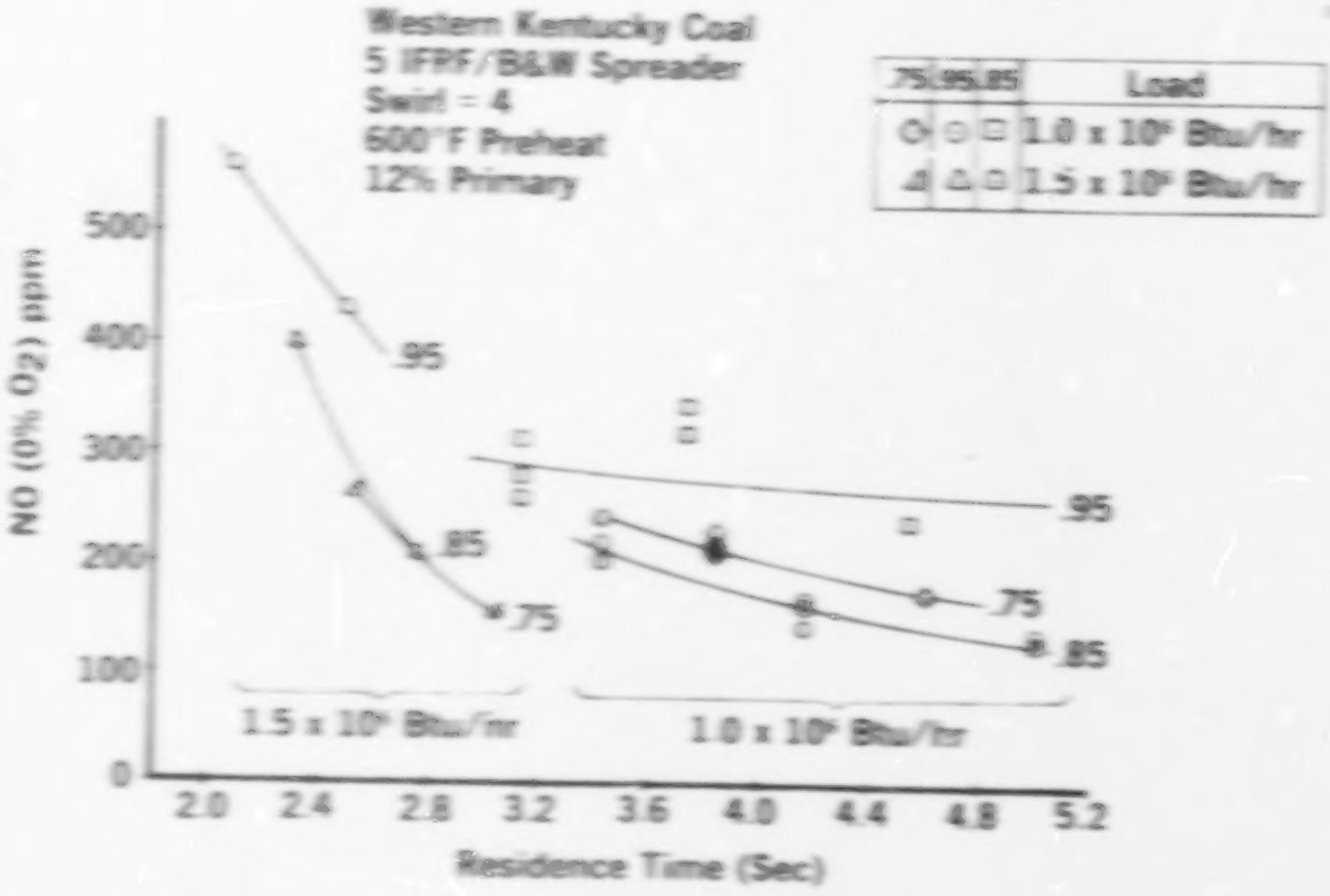


Figure 33. Effect of residence time - front wall fired.

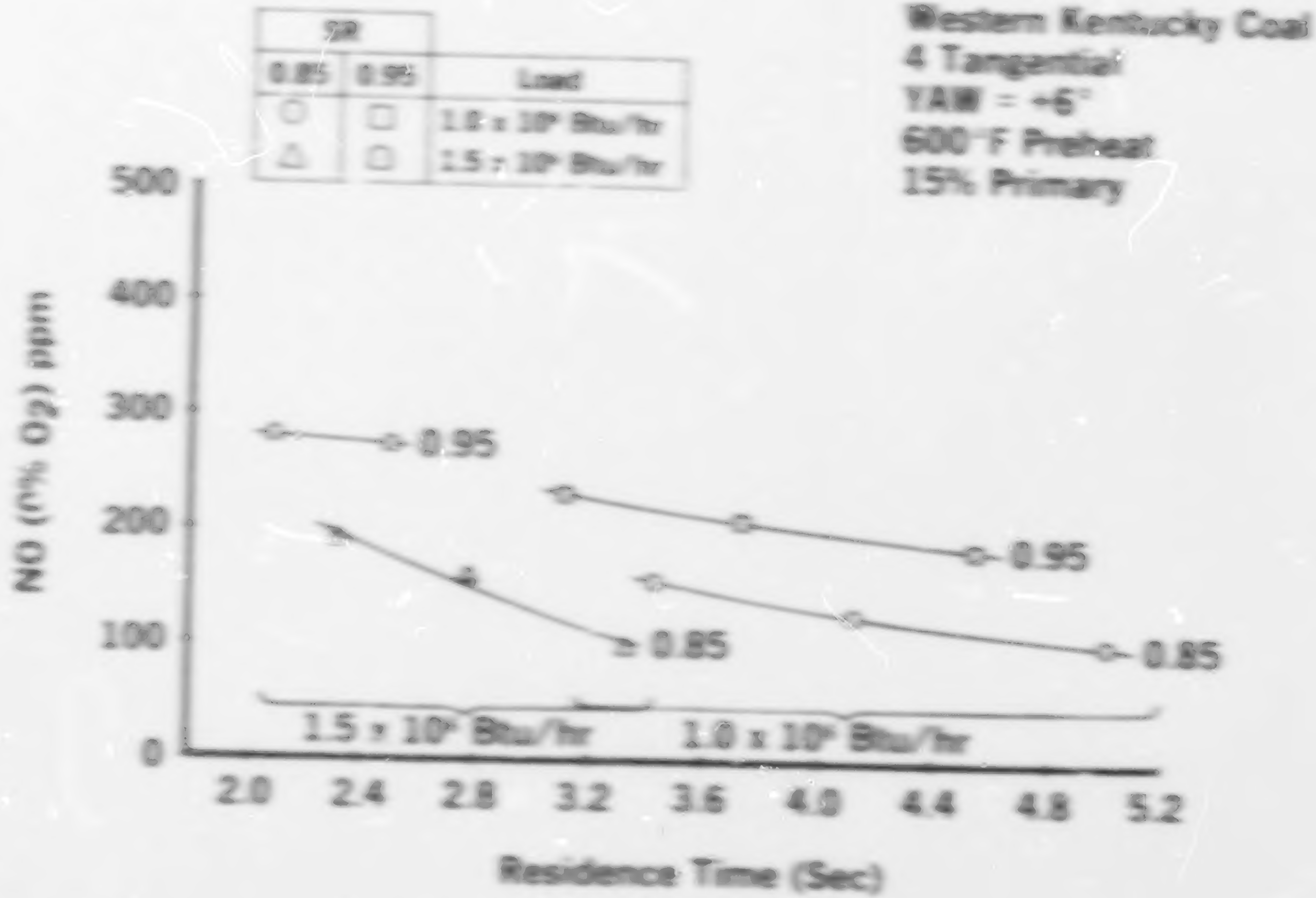


Figure [illegible]. Effect of residence time – tangentially fired.

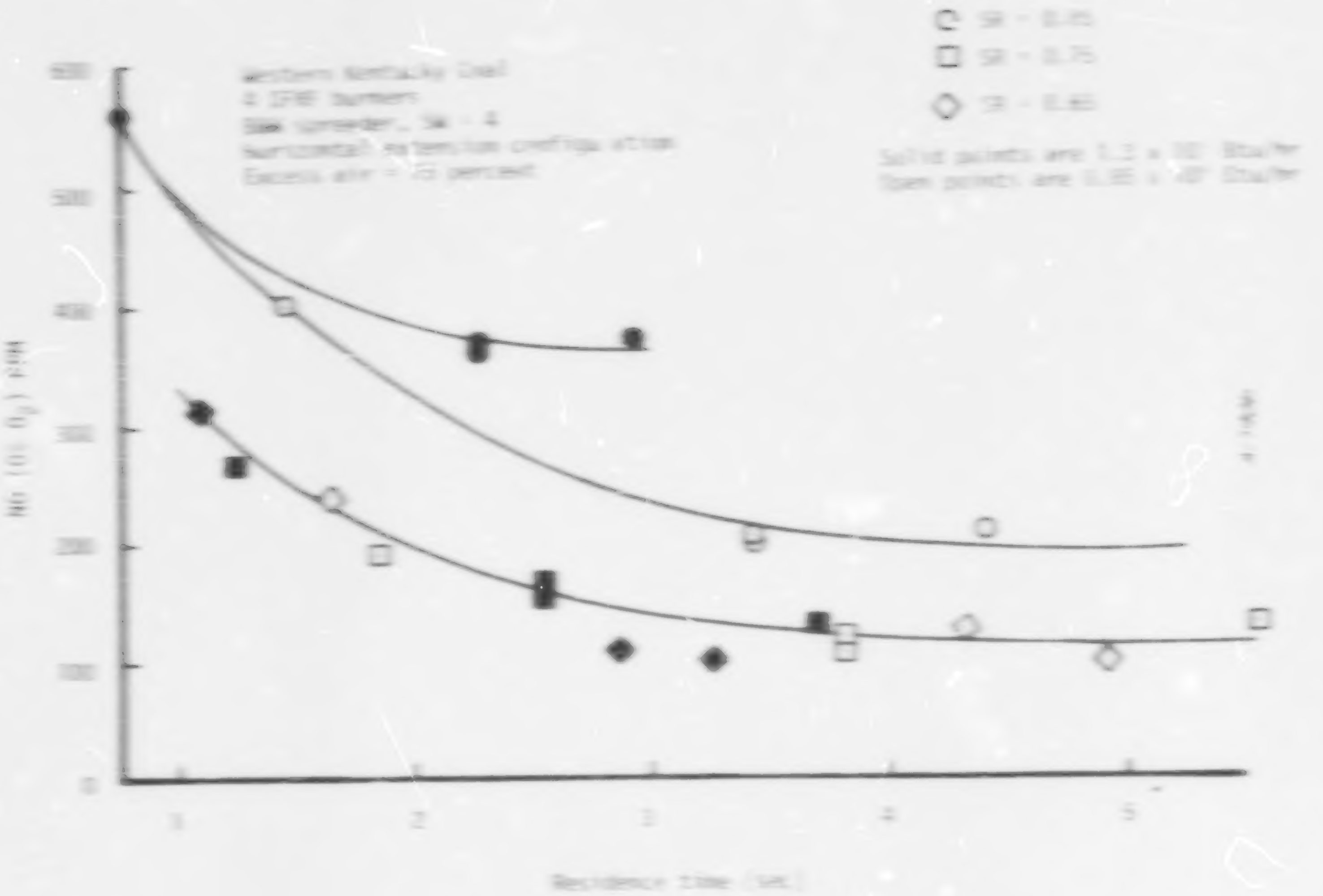


Figure 75. Stack NO vs. residence time to stage air addition.

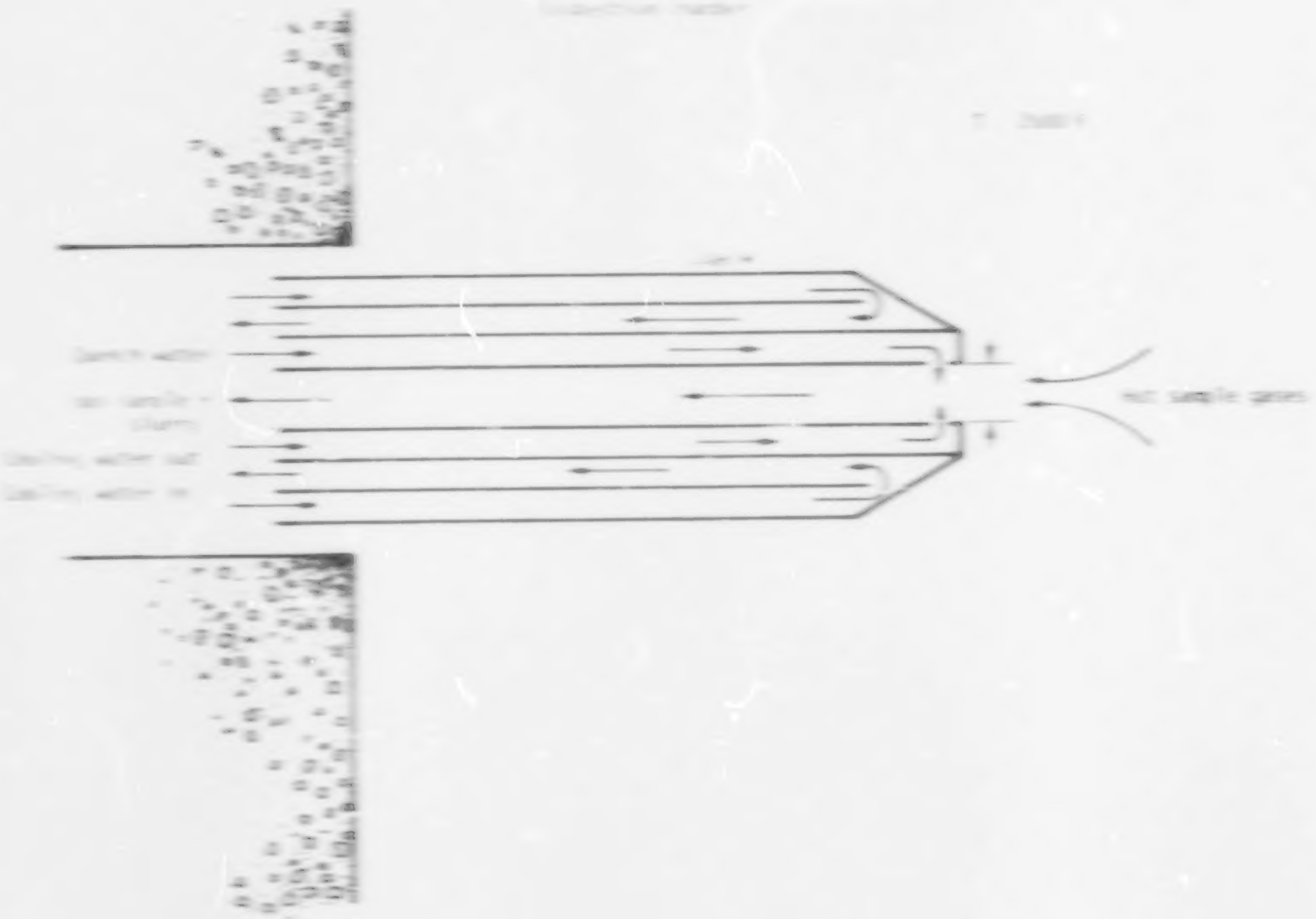

Combustion chamber
Quench water
Hot sample + slurry
Cooling water out
Cooling water in
Hot sample gases

Figure 16. Hot sampling probe.

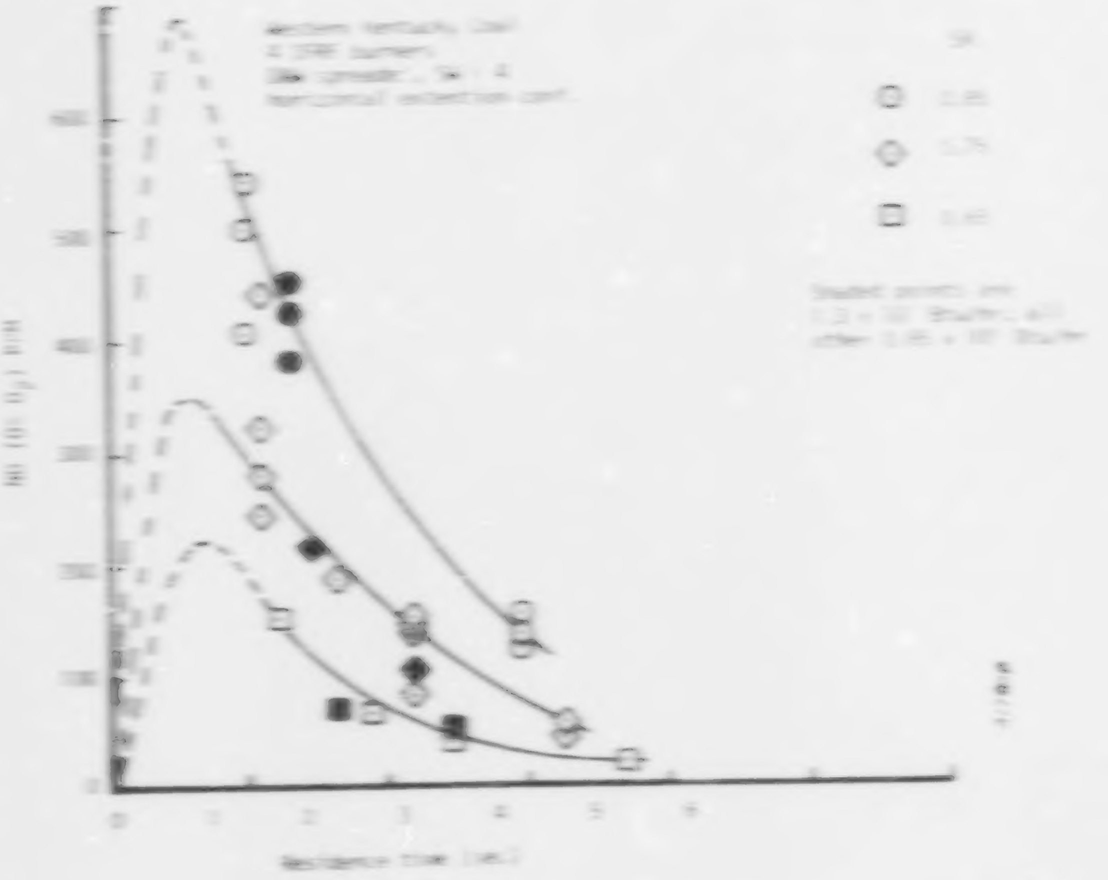


Figure 17. NO versus residence time in the first stage.

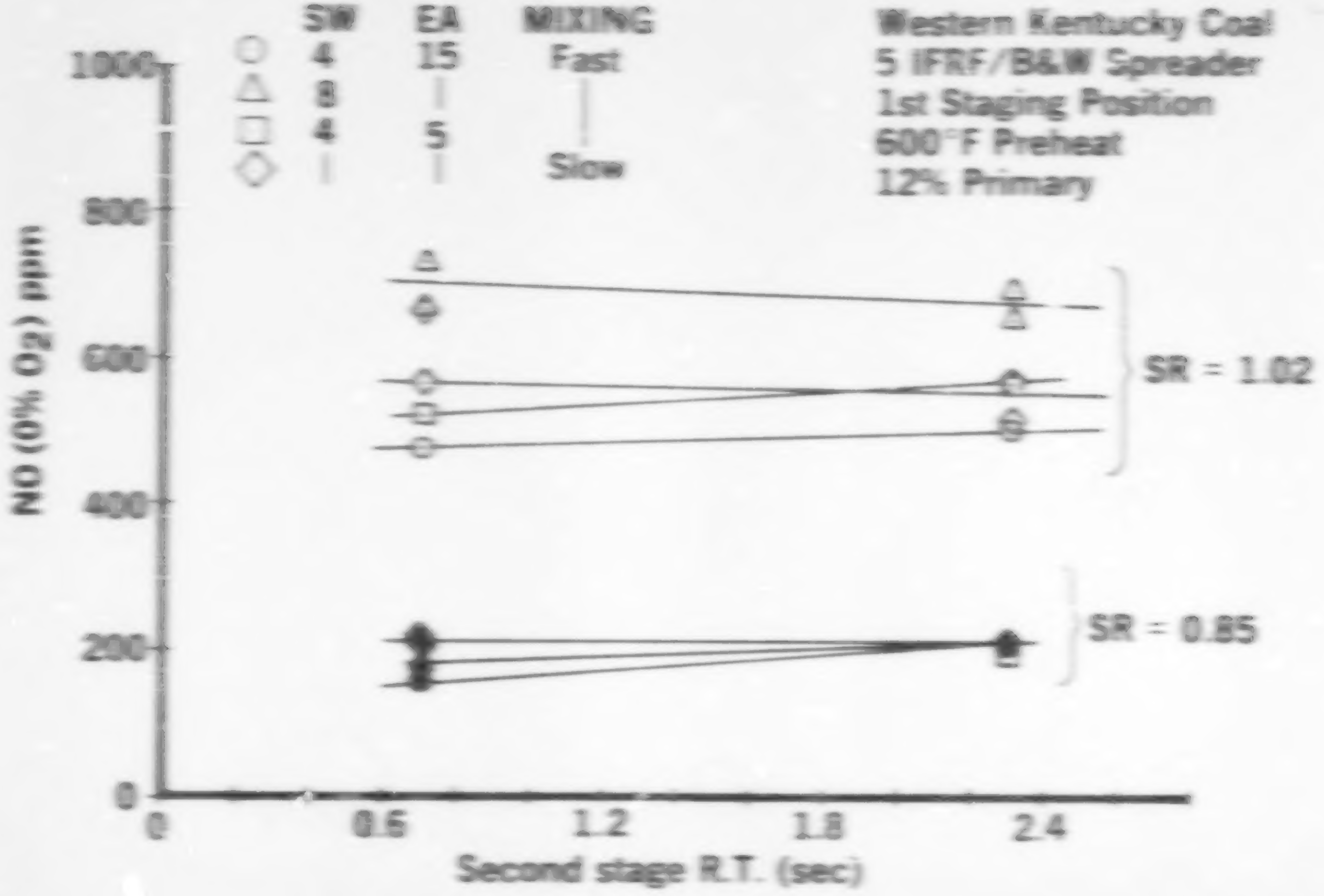


Figure 18. Effect of second stage residence time.

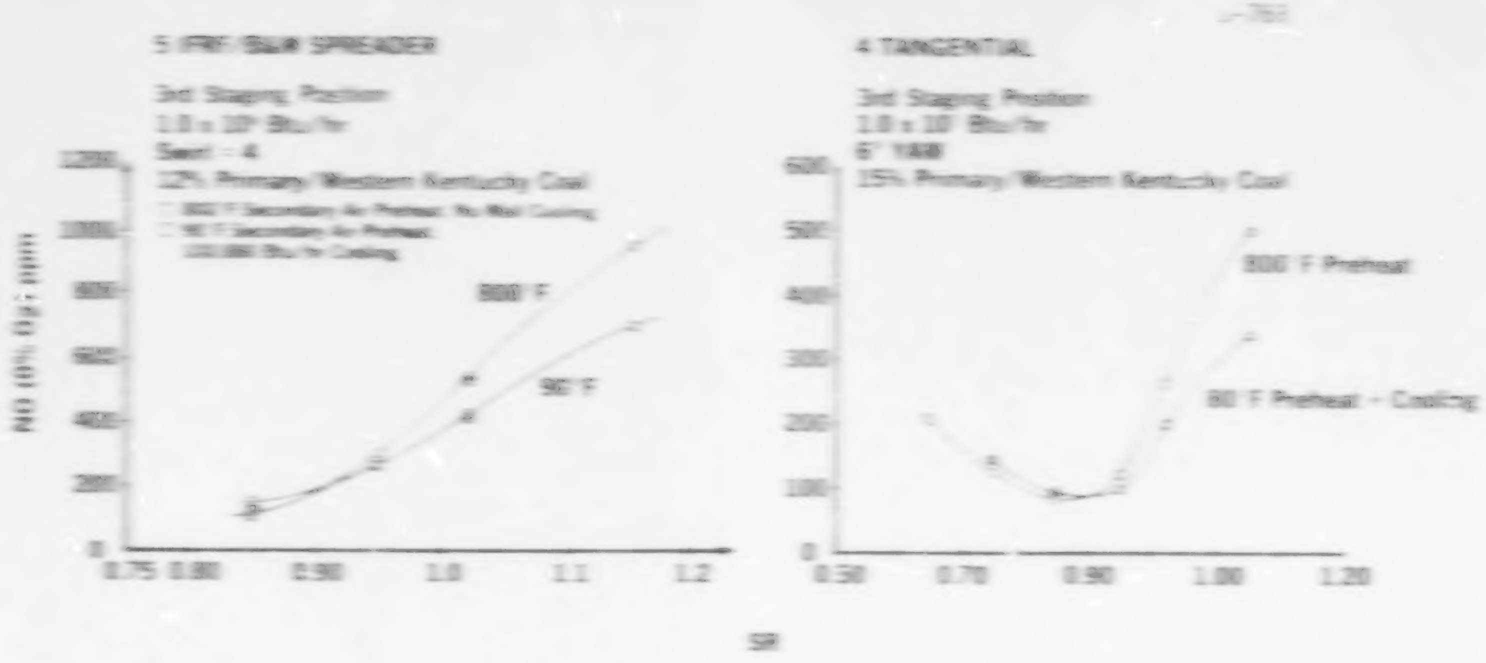


Figure 78. Effect of temperature.

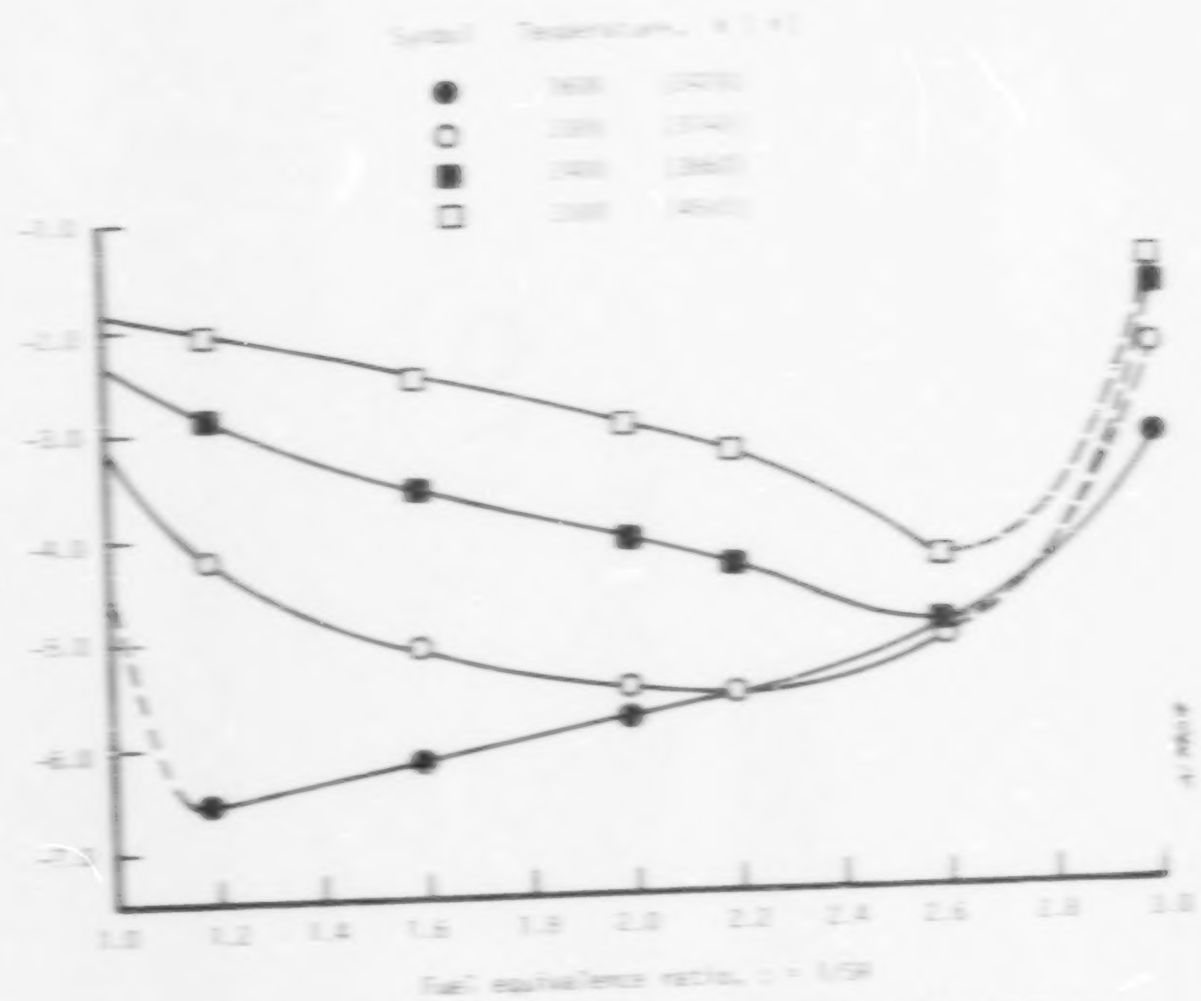
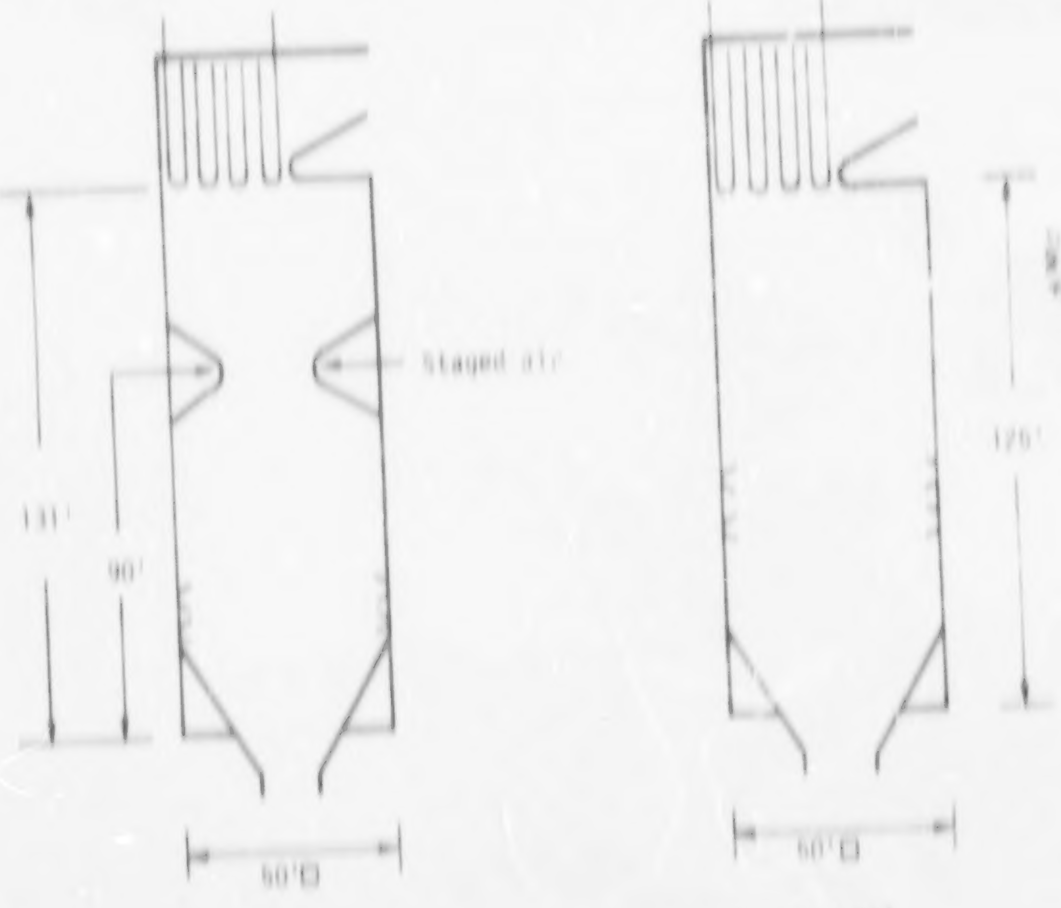


Figure 20. Sum of fixed nitrogen species mole fractions at equilibrium as a function of fuel equivalence ratio and temperature. Sarofim (26) (fuel composition = $CH_{1.3}$).

500 MW = 4.376 x 10^9 Btu/hr


131'
90'
Staged air
125'
50'□
50'□

Staged
SR_1 = 0.75
EA = 15 percent
τ_1 = 3.5 seconds
τ_2 = 1.3 seconds

Conventional
HR = 14000 Btu/hr·ft^2
EA = 15 percent

Figure 21. Candidate advanced staging design compared to conventional.

DESIGN CRITERIA FOR STATIONARY SOURCE CATALYTIC COMBUSTORS

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ABSTRACT

The use of catalysts in place of conventional burners for promoting hydrocarbon oxidation reactions appears to have advantages in the control of emissions. In addition, it is possible to achieve high system efficiency through appropriate system design, while holding the catalyst bed temperature to its operating limit. The objective of this program is to produce a new combustion system capable of extremely low emissions performance at the highest system efficiency achievable.

Design criteria for catalytic combustors include information on the catalyst/washcoat/substrate, the catalyst life, the preheat requirement for combustion air, and the maximum flow velocity and bed temperature that can be achieved in the system. Based on the results of an extensive catalyst screening program, an extremely active and durable catalyst system has been developed. The system, called the graded cell catalyst, incorporates three 1-inch long sections of alumina with varying cell diameters in a 3-inch bed. The catalyst used was platinum with a loading varying from 5 percent to 1.7 percent by weight. This system was tested at bed temperatures between 2,000°F and 2,700°F with four fuels (natural gas, propane, indolene, and methanol) under both rich and lean combustion conditions for a total test time of nearly 80 hours. Excellent performance was obtained throughout the test period; typical emissions at 217 percent theoretical air and space velocity of 97,600 $ft^3 hr/ft^3$ are 17 ppm CO, 10 ppm UHC, and 2 ppm NO_x. The graded cell catalyst system is now being incorporated into several combustion system designs.

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INTRODUCTION

Using catalysts in place of conventional burners to promote hydrocarbon oxidation reactions appears to help control emissions. The operating conditions of these catalytic combustors are limited by the catalyst bed temperature capability. The temperature obtained with normal one-stage, low-excess air operation (necessary for efficiency reasons) is above the temperature capability of current catalyst systems. Even if catalyst materials could withstand these temperatures, excessive NO_x emissions would be expected. It is therefore necessary to consider system techniques such as bed cooling, exhaust gas recirculation, or staged combustion to hold the bed temperature down. Appropriate system design will produce the two principle benefits of catalytic combustion: reduced emissions and increased system efficiency.

In this paper we describe the research and development program to establish catalyst and combustion system design criteria for the application of catalytic combustors to low emission, high efficiency stationary combustion systems. This program reviews available catalyst materials and ongoing research programs, and develops a basic understanding of the operation of catalytic combustion systems, small-scale catalyst screening experiments, and system concept tests. Based on these results, scale-up of the catalyst and catalytic combustion system will be accomplished. Prototype hardware designs utilizing catalytic combustors will be based on the design criteria established in this program.

AVAILABLE CATALYST MATERIALS

The materials considered for a catalytic combustion system are those associated with the support, the washcoat, and the catalyst itself. The importance of each of these elements in the system is described below.

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Support Materials

The catalytic support serves two important functions in a catalyst system:

- It increases surface area of the active metal or metal oxide by providing a matrix that stabilizes the formation of very small particles
- It increases thermal stability of these very small particles, thus preventing agglomeration and sintering with consequent loss of active surface area.

Monolith supports were developed for catalysts to provide a high geometrical surface area and a low pressure drop during operation. Monolithic supports are composed of small parallel channels of a variety of shapes and sizes. These structures may be in the form of honeycomb ceramics extruded in one piece, oxidized aluminum alloys in rigid cellular configurations, or multi-layered ceramic corrugations. The channels in honeycomb-like structures have tubular diameters from 1 to 7 mm. Materials of fabrication are usually low surface area ceramics such as alumina (Al_2O_3), mullite ($3Al_2O_3 \cdot 2SiO_2$), or cordierite ($2MgO \cdot 5SiO_2 \cdot 2Al_2O_3$). The refractory monolith is produced with macropores (1 – 10μ), and may be coated with thin layers of washcoat and/or catalytic materials. Figure 1 shows square-celled extruded monolith structures produced by Corning Glass Works.

Washcoat Materials

For conventional catalytic applications, the low surface area of the monolith structure requires the application of a thin oxide washcoat such as Al_2O_3. This washcoat, which strongly adheres to the ceramic or refractory support, provides a uniform high surface area while still insuring that the catalytic material subsequently impregnated on the washcoat is close to the main flow of reactants.

Under the high temperature (1100°C – 1500°C) conditions associated with catalytic combustors, a significant loss in washcoat surface area is expected. This loss in surface area results in pore closure, and can bury active catalytic sites. To minimize this problem, it is possible to work with catalysts which are deposited on presintered Al_2O_3. Alternatively, more thermally resistant washcoats, such as ZrO_2 or ThO_2, can be investigated. Finally, it may be possible to use no washcoat, if catalytic activity can be maintained when the catalyst is deposited directly on the monolith.

Catalyst Materials

Two broad classes of catalyst materials are available: metals and metal oxides. The metals of catalytic interest are listed in Table 1. Of these metals, the only ones which will remain in the metallic state in a high-temperature oxidizing environment are the noble metals; the others readily form oxides. Of the noble metals, a large volume of data and correlations are available for platinum and palladium at temperatures below 1000°C because of their use as automotive oxidation catalysts. They are among the most active catalysts for the oxidation of a number of fuels, including methane, methanol, and hydrogen. Palladium and platinum are readily prepared in a highly dispersed form on support materials. The use of the other noble metals is restricted to small quantities in multimetallic systems.

There has been much research on the catalytic properties of nonnoble metal oxides. As for noble metals, it has been found that the activity for hydrocarbon oxidation is increased at high-temperature operation. The most active single oxides are Co_3O_4, MnO_2, NiO, CuO, Cr_2O_3, Fe_2O_3, and V_2O_5. SiO_2 and Al_2O_3 have also been shown to have good activity at high temperature. Multicomponent metal oxides are also of interest.

The choice of an optimum catalyst/washcoat/support combination requires a consideration of the system's temperature capability. The low temperature limit is dictated by the lightoff temperature. Noble metal catalysts generally exhibit good lightoff characteristics for most fuels of interest, and would therefore be included in the lightoff system.

The major limitation for catalytic combustion is the high temperature of operation. Loss of catalytic activity through sustained operation at high temperature will occur with all catalysts, but this activity degradation should decay with time until a steady-state catalytic activity is reached. The support material is chosen to minimize thermal expansion problems at high temperatures, and to provide a high use temperature.

FUNDAMENTALS OF OPERATION

Catalytic combustion in a monolith bed is a complex interaction of chemical reactions (surface and gas phase), diffusive heat and mass transport (laminar or turbulent), convection, bed conduction, and radiation. These phenomena are depicted schematically in Figure 2. During steady operation, this process can best be described as follows:

- Premixed fuel and air are introduced into the combustor
- These gases diffuse to the surface of the combustor and react on the active sites at and within the surface
- Heat is generated and transferred by conduction, radiation, and convection. Part of this heat will be transferred to the main flow of gases and thermally support gas phase reactions.
- Surface reaction products diffuse back to the main flow of gases and are carried downstream.

If the heat release rate due to reaction at the surface is sufficiently great compared to convective, conductive and radiative heat losses, then the catalyst bed will operate in the "hot" mode. This type of operation gives significant fuel conversion whose magnitude is primarily controlled by mass transfer to the surface. However, if the surface reaction heat release is less than the heat losses, little temperature rise and fuel conversion is noted and the bed is said to be in a "blowout" condition. It is very important to know when this blowout condition occurs for a given catalyst system.

The overall fuel conversion within the catalyst bed is also very important. It is vital that sufficient residence time be given to the fuel/air mixture to allow diffusion and nearly complete reaction at the catalyst surface. This can usually be achieved by lengthening the catalyst bed or by decreasing the space velocity of the mixture. Gas phase reactions also contribute to the fuel conversion efficiency. These gas phase reactions are most efficient at high gas phase temperatures.

Graphical Determination of Stable Surface Combustion States

For the purpose of understanding system characteristics, considerable simplification of the catalytic combustion process can be made if it is assumed that:

- No conductive or radiative heat transfer occurs
- The Lewis number is unity for all species
- The combustion reaction can be described by an Arrhenius law equation

Once these assumptions are made, it is possible to perform a simple mass balance on the lean reactant at the wall of the monolith bed; that is, the mass of lean reactant transported to the wall is equal to the mass of lean reactant consumed at the wall. In equation form this can be written as

$$\dot{m} = Nu \frac{\rho \mathcal{D}}{D} (K_E - K_W) = AK_W e^{-\Delta E/RT_W}$$

where $\dot{m}$ = mass of lean reactant transported to and consumed at the wall, per unit area

Nu = Nusselt number for mass transfer (Sherwood number)

ρ = gas density

$\mathcal{D}$ = diffusion coefficient

D = diameter of one channel of monolith bed

K_E = mass fraction of lean reactant at boundary layer edge

K_W = mass fraction of lean reactant at monolith wall

A = preexponential factor

ΔE = activation energy

R = universal gas constant

T_W = temperature at monolith wall*

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*Based on the first two assumptions, this temperature can be related to the residual concentration of lean reactant at the surface, K_W.

Each of these expressions for the mass flux can be shown graphically by plotting the mass flux vs. the mass fraction of lean reactant at the monolith wall (i.e., plot $\dot{m}$ vs. K_W). This is shown in Figure 3.

By combining the two curves on a single graph, solutions to the problem may be identified as intersections of the two curves. The blowout condition may also be identified from this graphical solution.

The Graded Cell Concept

As shown in Figure 4, there are generally three solutions that can exist: a hot stable solution, an unstable solution, and a cold stable solution. The blowout point can be considered as that value of $\dot{m}$ where the hot stable solution and the unstable solution coincide; any increase in mass throughput above this value will cause the combustion reaction to be extinguished, i.e., the reaction is "blown out." A large value of $\dot{m}$ at blowout is desirable; it allows the monolith bed to operate at a large value of volumetric heat release rate, thereby minimizing the combustion volume required. As shown in Figure 4, to avoid blowout the intercept $Nu(\rho \mathcal{D}/D)K_E$ should be low. For a given surface activity of the monolith, blowout can therefore be avoided by:

- Using large diameter cells in the bed
- Operating at a high value of boundary layer edge temperature
- Operating at a small value of Nusselt number

The simplest of these to implement is the use of large diameter cells. These large cells operate at a low transfer coefficient and should be effective for both lightoff and sustained operation.

However, using large cells throughout the bed would result in poor conversion of combustibles to products. The amount of conversion is directly related to the number of transfer units in the bed, where the length of each transfer unit is equal to $Pr \cdot Re/4\,Nu \cdot D$,

where Pr = Prandtl number

Re = Reynolds number

Nu = Nusselt number

D = cell diameter

Thus, to get complete conversion, it is necessary to have many transfer units available by minimizing the length of each transfer unit. This suggests use of small diameter cells. The small cells will also accelerate homogeneous reactions, which are helpful for full conversion.

As a consequence of these operational fundamentals, it appears that a catalytic monolith bed used for the purpose of combustion should use large diameter cells at the front of the bed to prevent blowout, and small diameter cells at the back of the bed to maximize the number of transfer units in a given length of bed. Therefore, for a given catalyst, it was postulated that superior performance can be obtained by using that catalyst in a graded cell configuration, with large cells at the front end, small cells at the back end, and perhaps one or more intermediate sized cells between.

CATALYST SCREENING TEST PROGRAM

The initial series of combustion screening tests were conducted at the Jet Propulsion Laboratory in Pasadena, California. The objective of these tests was to evaluate the ability of a variety of catalyst/washcoat/support combinations to combust both gaseous and liquid fuels. Suitable combustion catalysts were identified based on the following characteristics:

- Low lightoff temperature
- Low preheat requirement for sustained operation
- Uniform catalyst bed temperature for a variety of test conditions
- High heat release capability
- Low pollutant potential
- High operational temperature capability
- Operation with both gaseous and liquid fuels
- Sufficient life for testing purposes

The initial screening tests identified catalyst properties which are important to each of these combustion characteristics. These tests utilized single-component supports that were 9.3 cm in diameter and 7.6 cm in length.

A screening test matrix was developed to compare monolith material, monolith cell size, washcoat material, washcoat application technique, catalyst, catalyst loading, and catalyst preparation technique. The primary test fuel used for this matrix was natural gas, with propane serving as a secondary test fuel. Table 2 gives a summary of the materials tested during the screening program.

Prior to combustion testing, all catalysts were characterized in a high vacuum gas adsorption system in terms of total and selected (precious metal dispersion) surface area. The catalyst characterization system is shown in Figure 5. The system consists of three major components: (1) the pumping and vacuum control system, (2) the gas delivery, storage, and cleaning system, and (3) the working volume and characterization cells. Catalyst total surface area is determined by the BET gas adsorption procedure.

Following surface characterization, the catalysts were instrumented with in-depth thermocouples placed within monolith cells, as shown in Figure 6. Cells containing thermocouples were blocked off so the thermocouple would read ceramic surface temperature. Catalysts were then placed in a quartz reactor, as shown in Figure 7, and tested at JPL. The test procedure involved establishing initial lightoff temperature, operating the catalyst at minimum required preheat for flow conditions between 50 and 300 percent theoretical air, repeating data points periodically to check for catalyst degradation, and recording lightoff temperature as a function of time. Diluent nitrogen was introduced to maintain bed temperature constant at 1100°C. Data for test model JPL-010K, a platinum/alumina/cordierite catalyst system, are given in Table 3 and Figure 8.

As shown in Figure 8, the catalyst lightoff temperature increased from 330°C to 470°C after 10 hours of operation at a bed temperature of 1100°C. In addition, after 8 hours of testing, the preheat required at 150 percent theoretical air to sustain combustion reactions in the bed had increased from 50°C to 410°C. The increase in both lightoff and required preheat temperature indicates a significant decrease in catalyst activity. Further, from Table 3, a decrease in total surface area by a factor of twenty and a loss in platinum surface area to nearly zero shows significant sintering of both washcoat and catalyst.

To overcome performance degradation with time, higher catalyst loadings were used. These high loadings gave much higher catalytic activity after operation at high temperatures, allowing good performance even in the "degraded" state.

Based upon the results obtained from the screening test matrix, direction was gained to develop a catalytic combustion system with good combustion characteristics. Results from the screening tests showed that:

- Most catalysts tested had good initial activity, as compared to their activity after testing
- Degradation occurred rapidly at high temperature operation, resulting in higher required preheat to prevent blowout at a given value of theoretical air and fuel flowrate
- Increasing platinum loading gave significantly greater activity, even after high temperature operation
- Stabilizing the platinum by exposure to hydrogen sulfide during preparation gave improved performance
- Using presintered γ-alumina or α-alumina washcoats improved performance
- Alumina monoliths survived high temperature (1500°C) operation with minimal thermal shock
- Large diameter cells passed many unburned hydrocarbons but could not be blown out at the facility flowrate limits
- Small diameter cells provided excellent cleanup of CO and UHC

GRADED CELL CATALYST DEVELOPMENT

The graded cell catalyst was developed by combining the basic understanding of catalyst-coated monolith operation with the results of the initial screening tests. It combines features which result in high throughput capability without blowing out, and has consistent lightoff temperature, low emissions, and long life. The graded cell catalyst consists of three 2.5 cm long segments of ceramic with varying cell diameters. The largest cells are placed in the front of the bed to initiate surface reactions, intermediate cells in the center of the bed allow gas phase reactions to begin, and small cells at the back end perform cleanup of CO and UHC to extremely low levels. A photograph of a graded cell catalyst (Model 019) is shown in Figure 9. Table 4 summarizes the composition of Model 019.

Model 019 was initially tested at JPL in the 1-atmosphere quartz reactor. Natural gas, indolene, propane, and methanol fuels were tested under lean conditions at bed temperatures of 1100°C, followed by tests with natural gas and propane at 1320°C. This testing was quite successful; the catalyst was operated at the maximum flow capacity of the JPL system throughout the 50-hour test period. Table 5 summarizes data from the multifuel tests.

Following the multifuel tests, pressure and simulated fuel nitrogen conversion tests were run in the Aerotherm test facility shown in Figure 10. This facility can operate at up to 10 atmospheres pressure and 917 m^3/hr airflow. Combustion tests up to 6 atmospheres pressure were run successfully. Ammonia dopant was added to the methane fuel to simulate fuel nitrogen compounds, and tests run at 1100°C and 1320°C bed temperature to examine the conversion of ammonia to nitrogen oxide under both fuel-rich and fuel-lean conditions. On the rich side, most NH_3 was passed directly through the combustor unchanged. At 200 percent theoretical air, however, it was noted that increasing pressure through the bed (while maintaining flowrate constant) resulted in an increase in NH_3 conversion to NO_x from 25 percent to 70 percent of the dopant. This is attributed to a change in the dominant oxidation reactions from surface to gas phase at the lower pressure. Thus, a combustor which maximizes surface reactions may be capable of controlling the conversion of fuel-bound nitrogen to nitrogen oxides.

Test Model 019 was also operated with natural gas fuel to a maximum bed temperature of 1490°C. The catalyst performed well throughout the 78 hours of testing. Post-test analysis showed the catalyst had no measurable surface area or platinum dispersion, but identifiable platinum was found on the front segment using the scanning electron microscope and X-ray diffraction. Platinum on the back segment had agglomerated into large particles at the exit end of the bed

Lightoff temperature for this catalyst was very consistent at 455°C under fuel-rich conditions.

Additional graded cell catalysts are now being tested. W. R. Grace and Co. prepared a platinum/iridium catalyst which was tested at 1320°C and 1480°C bed temperatures. This catalyst was tested with natural gas fuel at 1 atmosphere pressure for a 20-hour period. Blowout tests demonstrated the catalysts' ability to accept high mass flowrate; a maximum volumetric heat release rate of 6.07×10^5 joules/hr-cm^3 was achieved at 1480°C bed temperature and 600°C preheat temperature. Again, post-test analysis showed no measurable surface area or precious metal dispersion.

Based upon the testing conducted to date, the graded cell catalyst system shows promise for operation at high bed temperatures for significant lengths of time. It appears suitable for the combustion of natural gas, propane, methanol, and indolene (distillate oil) with low emissions and high combustion efficiency. Limited data indicate that under certain operating conditions, the graded cell catalyst may help in controlling the conversion of bound nitrogen to nitrogen oxide. Testing of this system will be continued.

SYSTEM CONCEPTS

For most stationary source combustion systems, high system efficiency can only be achieved by operating at stoichiometric conditions. In order to hold temperatures below the allowable maximum for the catalyst, and to minimize the formation of nitrogen oxides through gas phase oxidation reactions, it is necessary to devise a system that minimizes operating temperatures and still provides highly efficient combustion with low emissions. Such systems as staged combustors or exhaust gas recirculation systems are complicated and somewhat expensive. The most effective method of heat removal from a catalytic combustor is by radiation, and the system described here is termed the radiative catalytic/watertube system.

Radiative Catalytic/Watertube System

The radiative catalytic/watertube system was designed to operate at stoichiometric conditions without exceeding the maximum operating temperature of the catalyst. A schematic of the system concept is shown in Figure 11. A stoichiometric fuel/air mixture enters the radiative section, where catalyst-coated cylinders are surrounded by watertubes. Reactions will begin at the surface of the catalytic cylinders, and as the cylinder temperature increases, it will begin to radiate energy to the watertubes. Some of the fuel will pass entirely through the bed unchanged; the degree of combustion in the radiative section is dependent on the number of transfer units in the bed. The partially-combusted gases are then mixed to provide a uniform mixture before they enter a graded cell catalyst adiabatic combustion section, and final heat removal is achieved in a downstream convective section before exhausting to the stack. This concept thus provides for "staged" combustion with no necessity of adding additional fuel or air downstream.

The radiative section was designed, constructed, and tested with natural gas at Acurex/Aerotherm. System pressure was 1 atmosphere, and data were taken to establish the effects of changes in load on radiant heat extraction, the minimum preheat required for operation, and the gas composition at the exit of the radiative section. The test apparatus is shown in Figure 12. The catalyst used was platinum on alumina-washcoated alumina cylinders.

Figure 13 compares the heat removed in the radiative section with the total energy available for different fuel flowrates. The system was designed to operate at a fuel flowrate of 4.3 kg/hr, to combust 40 percent of the fuel entering and to remove 30 percent of the total available energy by the watertubes. At the design condition, the amount of combustion was measured as 41.8 percent, with 25-percent energy removal in the watertubes.

Figure 14 shows the variation in catalyst surface temperature with distance in the radiative section. Even with the adiabatic flame temperature of the fuel/air mixture above 2000°C, the maximum surface temperature of the cylinders was only 1044°C. By maintaining the catalyst surface at a low temperature, catalyst life is significantly prolonged. No NO_x emissions existed in the combustion gases. Typical emissions which would enter the graded cell catalyst for total combustion include 17.4 percent O_2, 1.5 percent CH_4, 3000 ppm CO, and <0.2 percent CO_2.

The radiative catalytic/watertube system was successfully tested as a viable concept for direct bed heat removal. Such a system has application in commercial and industrial boilers, where low excess air is needed for high system efficiency. This concept will be further tested with the graded cell monolith, to establish a stoichiometric combustion system with minimal NO_x emissions.

SUMMARY

Significant progress has been made toward developing design criteria for stationary source catalytic combustors. Both the graded cell catalyst system and the radiative catalytic/watertube system have been tested and appear effective in controlling NO_x emissions. These devices have potential application in gas turbines and commercial and industrial boilers.

Further testing will be done with additional fuels and at higher catalyst surface temperatures. The formation of NO_x under high temperature heterogeneous combustion conditions is currently speculative, and needs to be examined.

TABLE I. NOBLE METALS OF INTEREST FOR CATALYTIC COMBUSTION

Group VIII*			Group IB*
Fe	Co	Ni	Cu
Ru	Rh	Pd	Ag
Os	Ir	Pt	Au

*Enclosed metals are considered noble.

TABLE II. SUMMARY OF MATERIALS TESTED IN SCREENING TESTS

Component	Variable Tested
Monolith	Cordierite, mullite, alumina
Washcoat	γ-Al_2O_3 (two types), presintered γ-Al_2O_3, stabilized γ-Al_2O_3 (two types), α-Al_2O_3
Cell size	7 mm, 5 mm, 3 mm, 1.5 mm
Cell shape	Hexagonal, circular, square
Catalyst	Platinum, platinum/palladium, oxide
Platinum loading	0.3%, 0.7%, 1.5%, 2%, 5%

TABLE III. CHARACTERIZATION SUMMARY - TEST MODEL JPL-D10B

Support: General Refractories cordierite; 31 circular cells per square centimeter

Washcoat: Oxy-Catalyst 10 wt percent γ-Al_2O_3

Catalyst: Aerotherm 0.75 wt percent platinum

Pretest characterization: Total (BET) surface area = 7.9 m^2/g
Dispersion = 94.1%

Post-test characterization: Total (BET) surface area = 0.4 m^2/g
Dispersion = 0.1%

TABLE IV. GRADED CELL CATALYST MODEL 019 COMPOSITION

Support: Three segments of DuPont Alumina, cell sizes
7 mm, 5 mm, 3 mm, hexagonal cells

Washcoat: DuPont alumina AA

Catalyst: Aerotherm platinum

Catalyst loading: 4.7 wt%, 2.6 wt%, 1.8 wt%, front to back

Catalyst Pretreatment: Hydrogen sulfide

TABLE V. GRADED CELL CATALYST MODEL III MULTIFUEL TESTS

Fuel	Theoretical Air, %	Space Velocity, hr^{-1}	Preheat Temperature, °C	Average bed Temperature, °C
Methane	220	88,200	514	1106
	208	74,500	451	1171
Propane	250	78,800	463	1083
	248	72,700	462	1120
Indolene	296	80,900	430	1066
Methanol	241	72,300	145	1055

NOTE: Very low emissions were noted for all tests.

Gaseous fuels showed more uniform bed temperature distributions than liquid fuels.

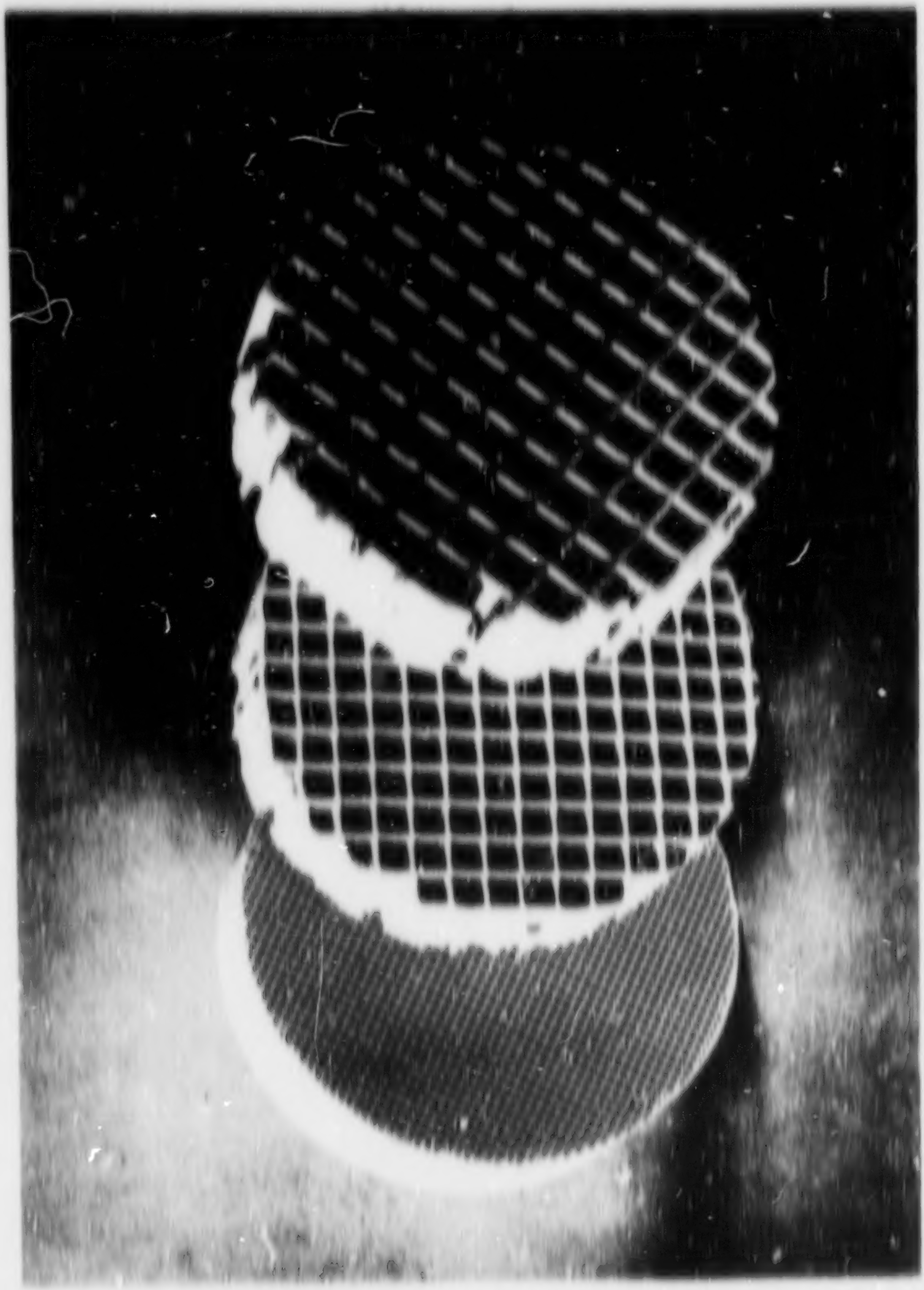

Figure 1. Corning square-celled extruded monolithic structures.

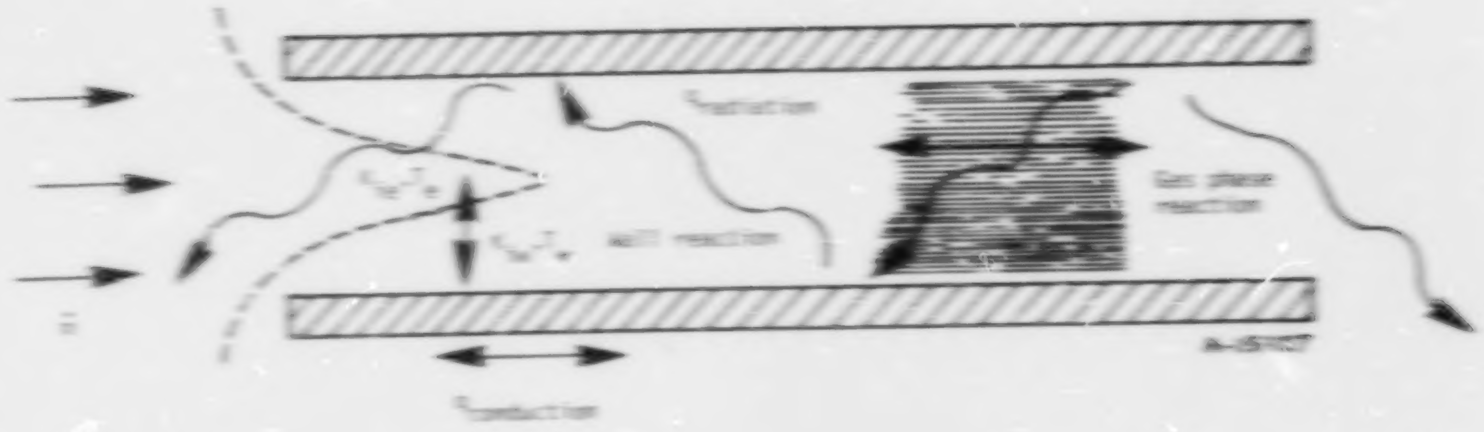
$q_{radiation}$
C_b, T_b
C_w, T_w
Wall reaction
Gas phase reaction
$q_{conduction}$

Figure 2. Physical events in a monolith cell.

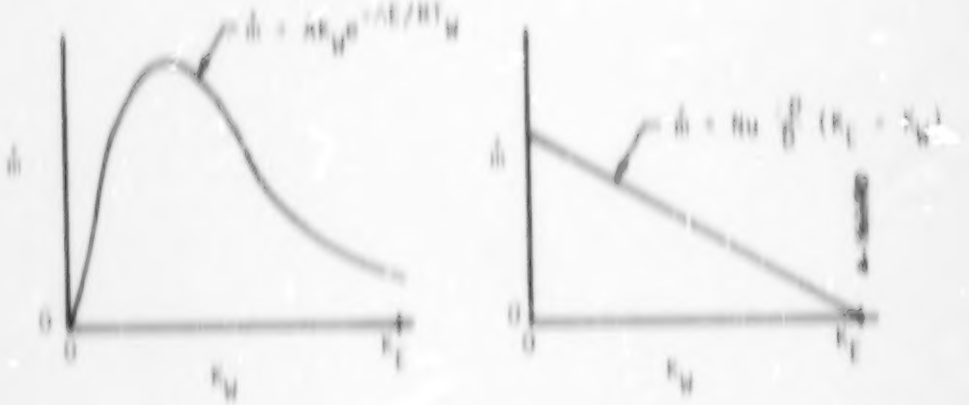

Figure 3. Mass flux as a function of mass fraction of lean reactant at the monolith wall.

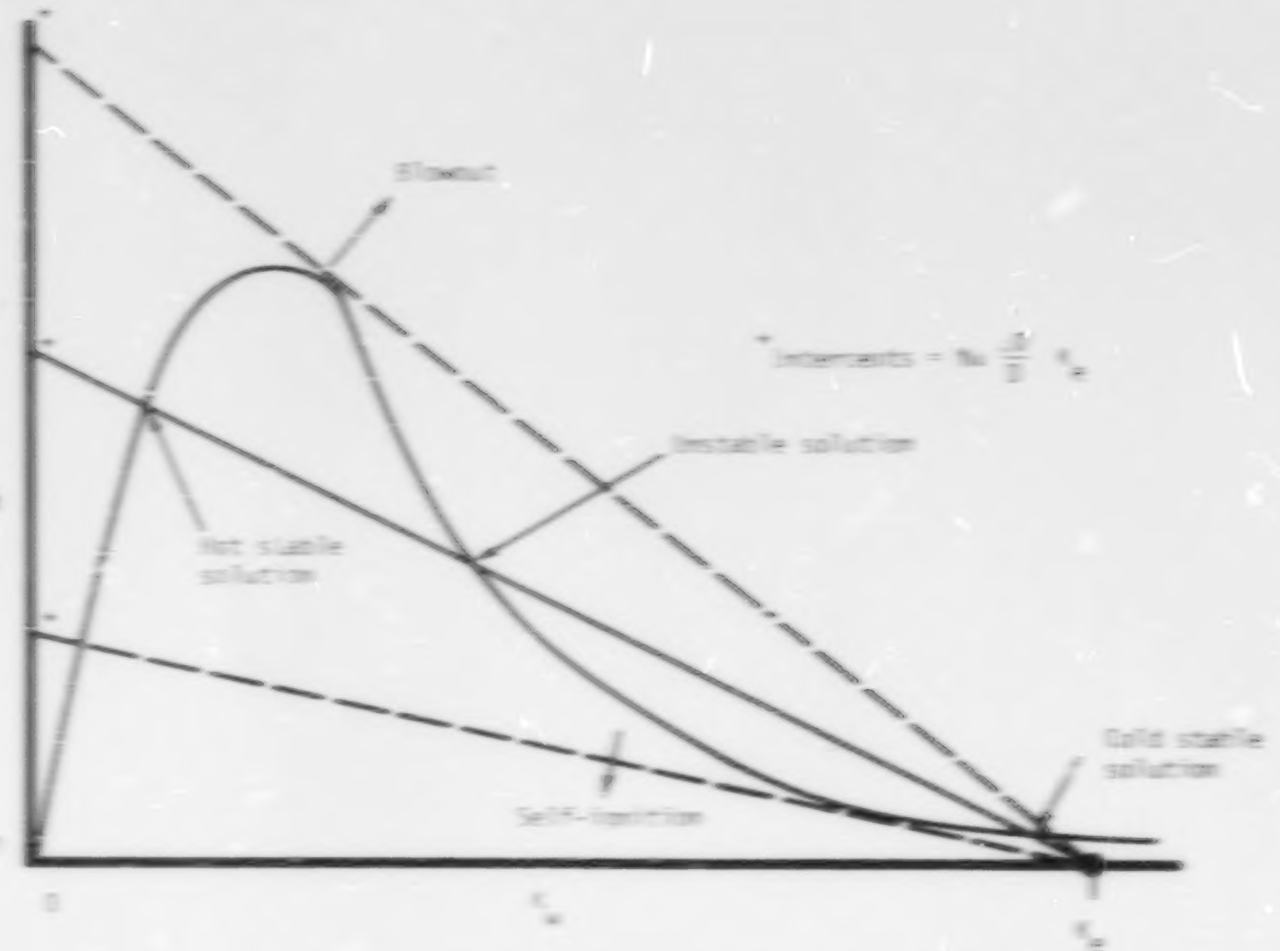
Blowout
* Intercepts = Nu $\frac{D'}{D}$ c_e
Unstable solution
Hot stable solution
Cold stable solution
Self-ignition
0
0
c_w
c_e

Figure 4. Simplified mass balance solution for catalytic combustor in a monolith bed.

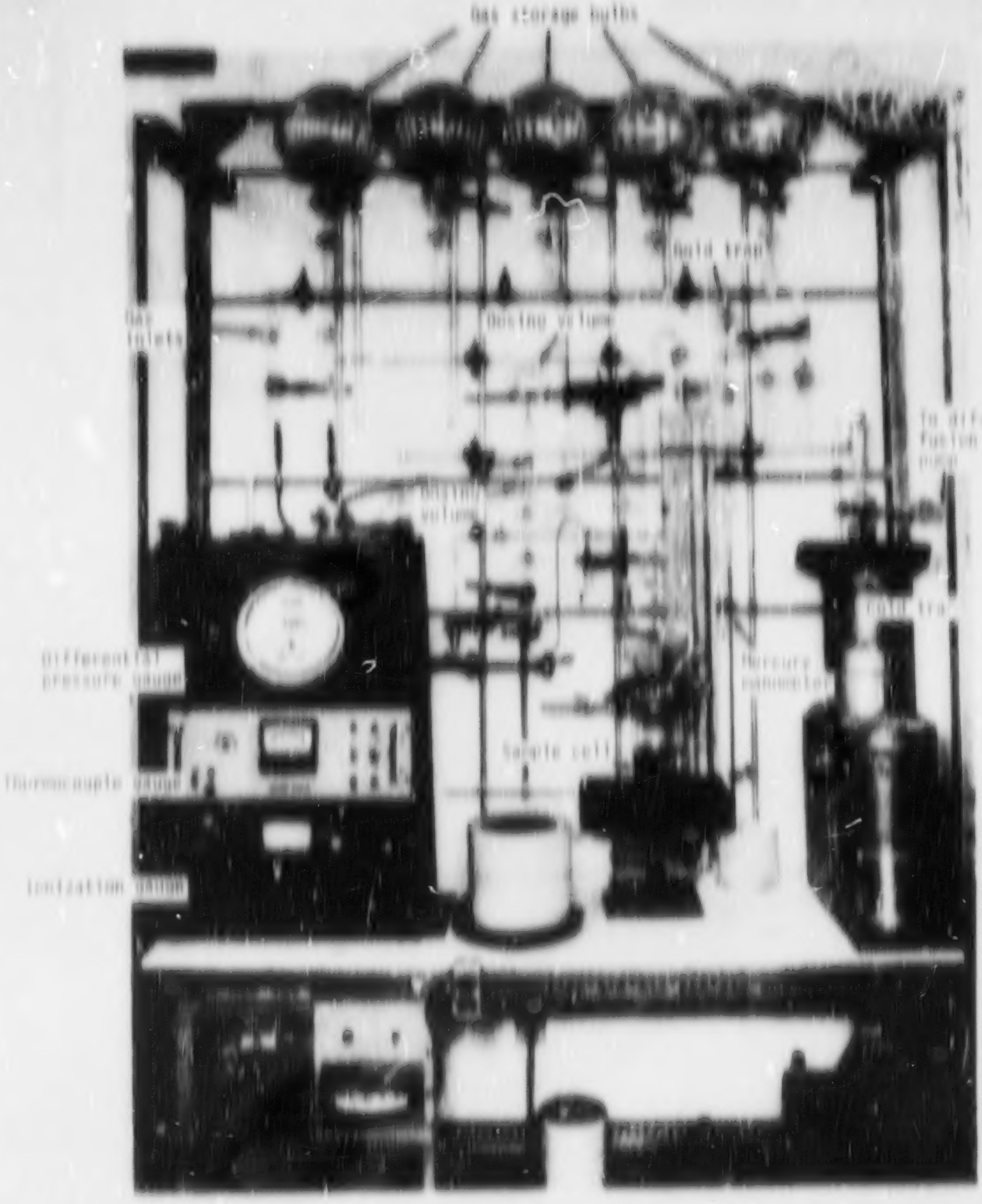
Gas storage bulbs
Cold trap
Gas inlets
Dosing volume
To diffusion pump
Dosing volume
Cold trap
Differential pressure gauge
Mercury manometer
Sample cell
Thermocouple gauge
Ionization gauge

Figure 5. Catalyst characterization system.

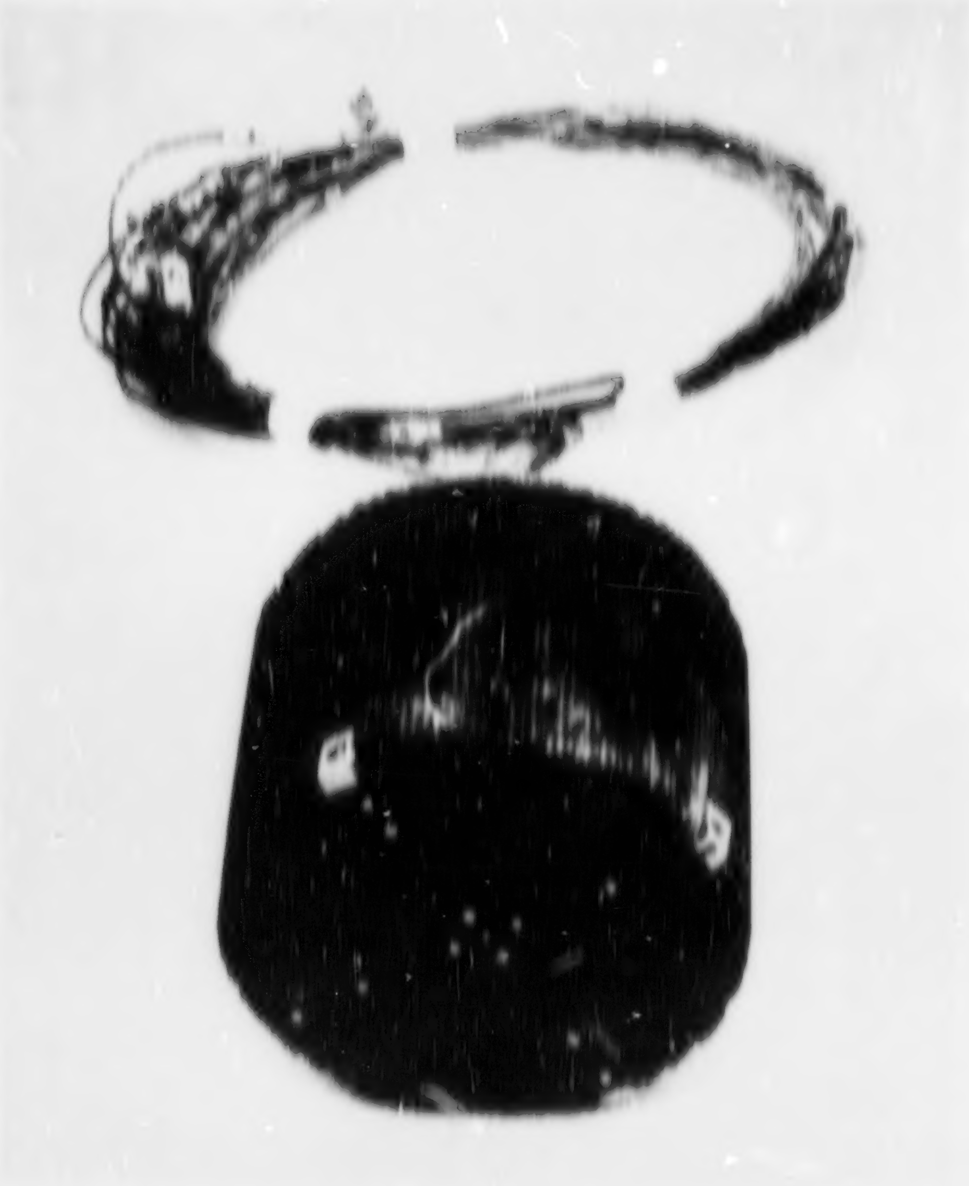

Figure 6. Model JPL-001, platinized cordierite with 30 thermocouples placed in monolith.

Figure 7. Quartz reactor with monolithic catalyst bed (one pound) and exhaust gas sampler.

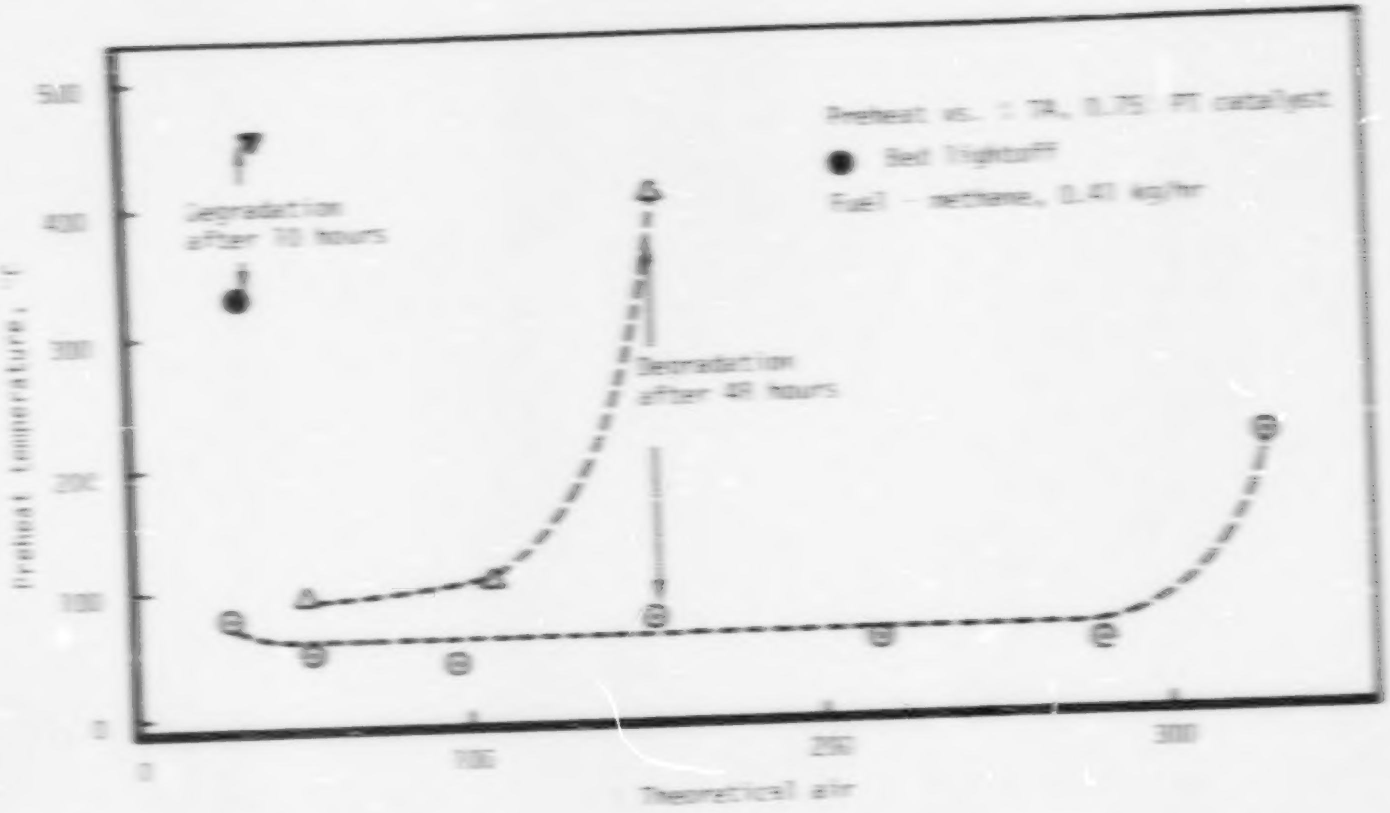

Figure 8. Preheat temperature required for operation as a function of theoretical air for test model JPL-010X.

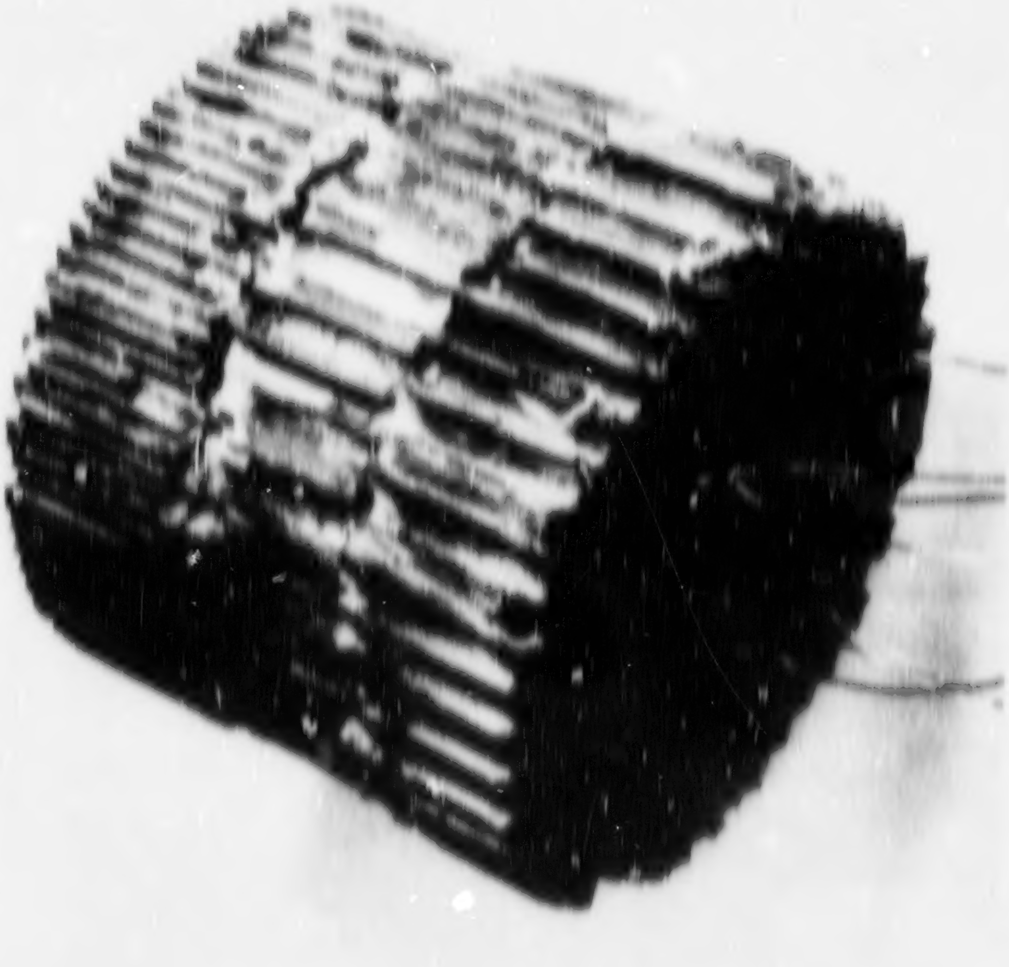

Figure 9. Aerotherm graded cell catalyst (Model 019) - front view.

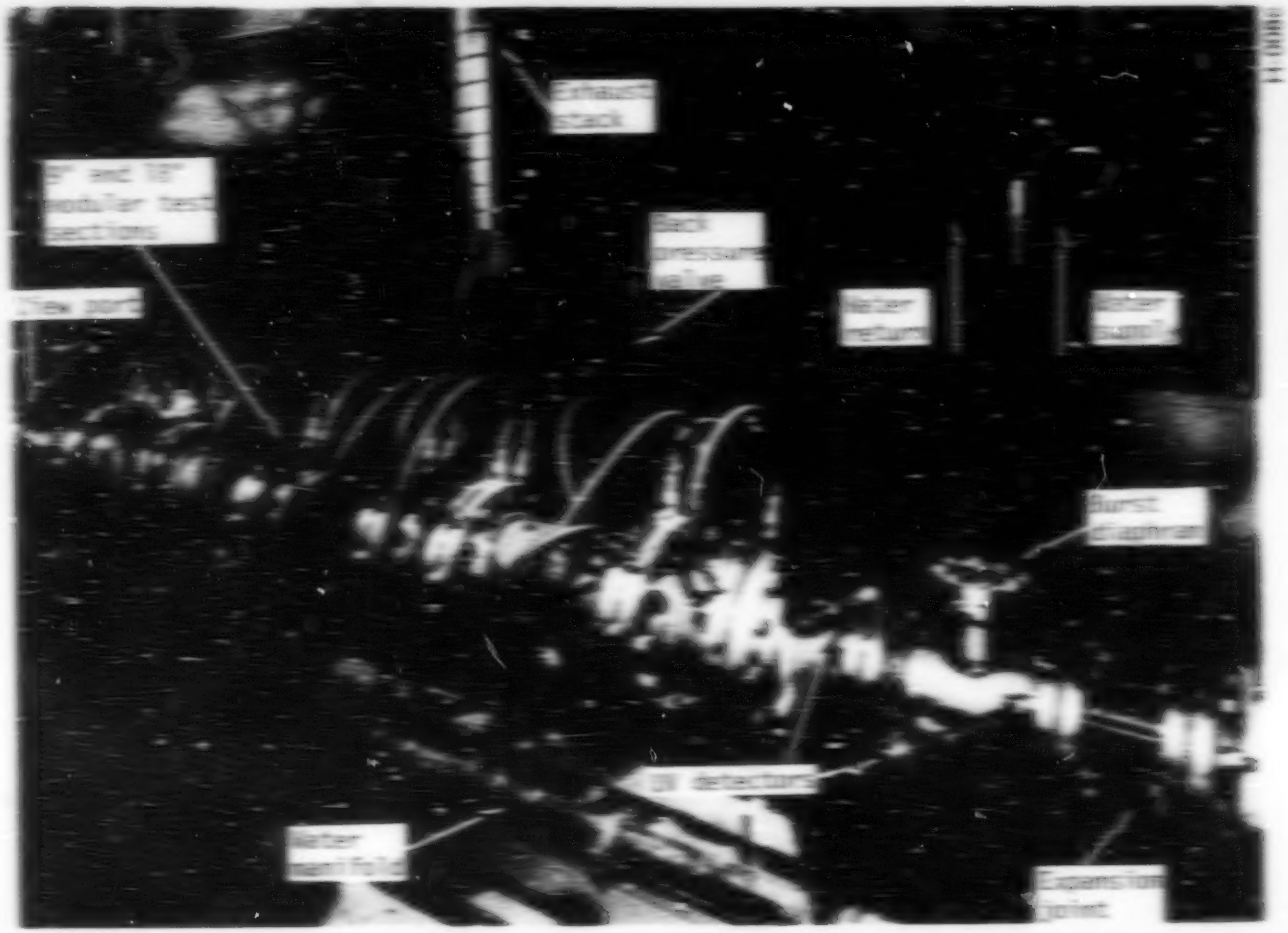
Exhaust stack
8" and 10" modular test sections
View port
Back pressure valve
Water return
Water supply
Burst diaphragm
UV detectors
Water manifold
Expansion joint

Figure 10. Aerotherm test section and exhaust systems.

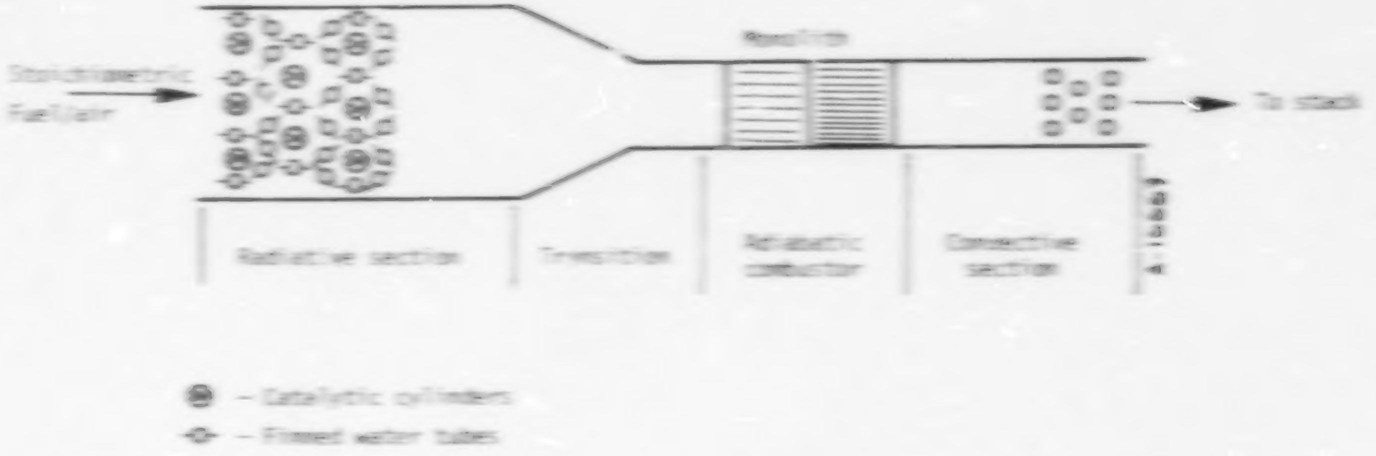
Stoichiometric
Fuel/air
Monolith
To stack
Radiative section
Transition
Adiabatic combustor
Convective section
A-16669
— Catalytic cylinders
— Finned water tubes

Figure 11. Radiative catalytic/watertube combustion system design concept.

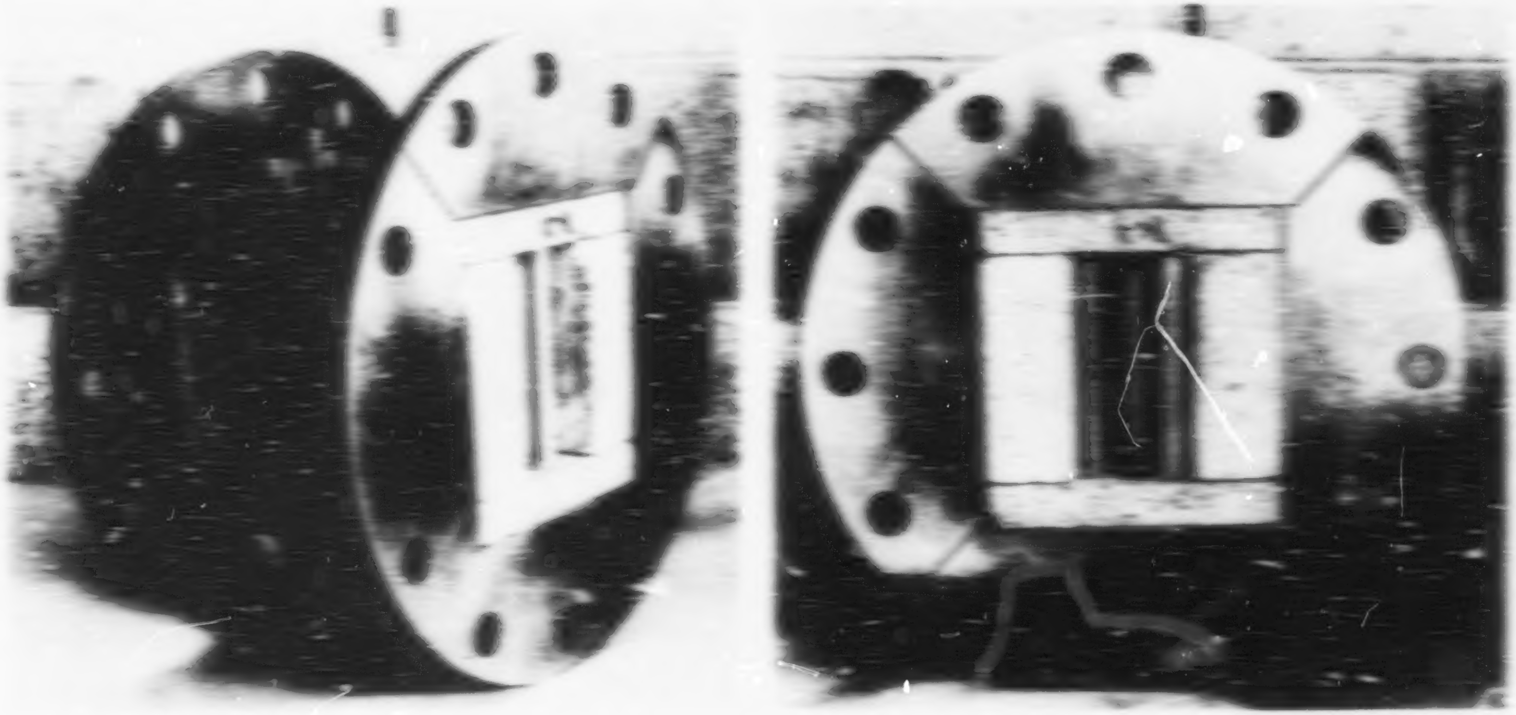

Figure 12. Radiatively-cooled catalytic combustor test apparatus.

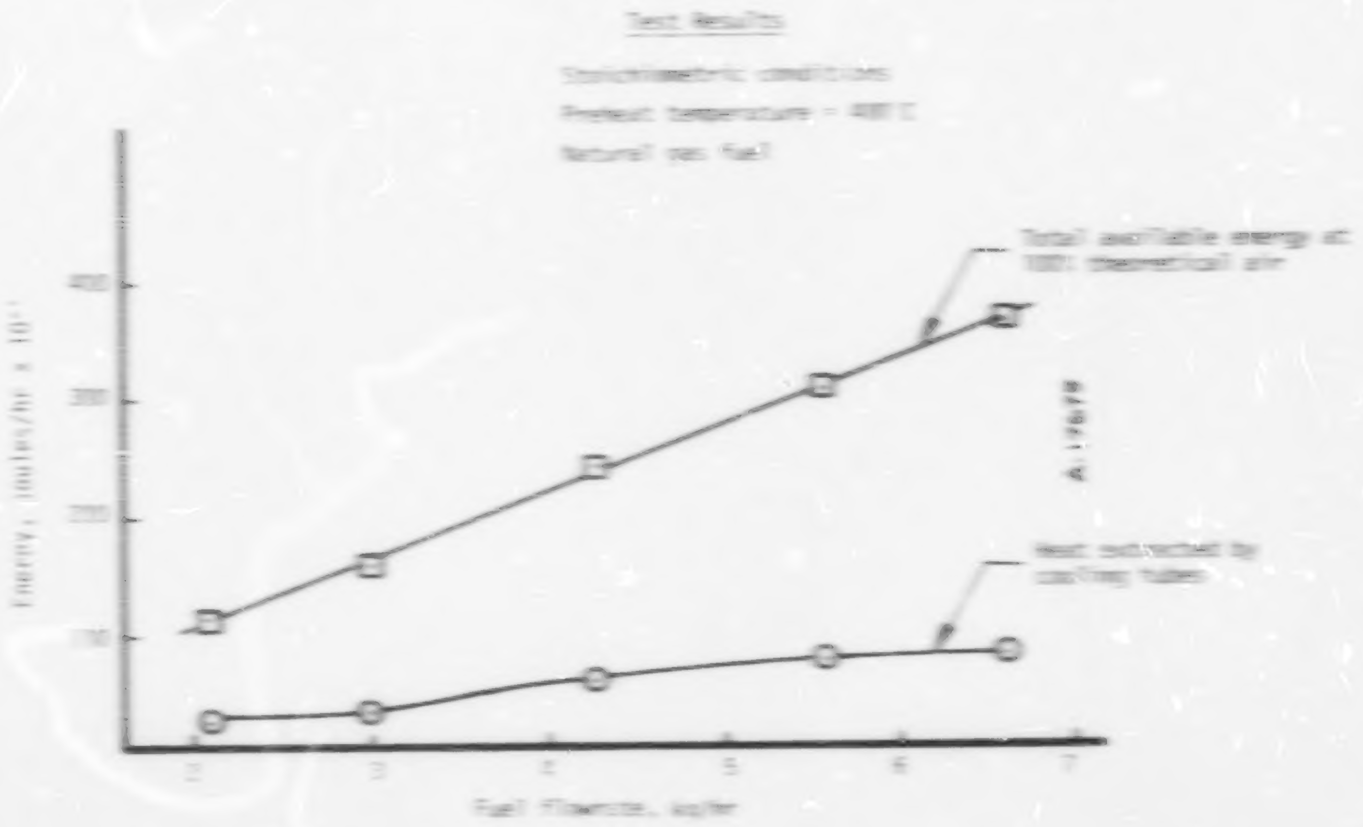

Figure 13. Radiative catalytic/watertube system.

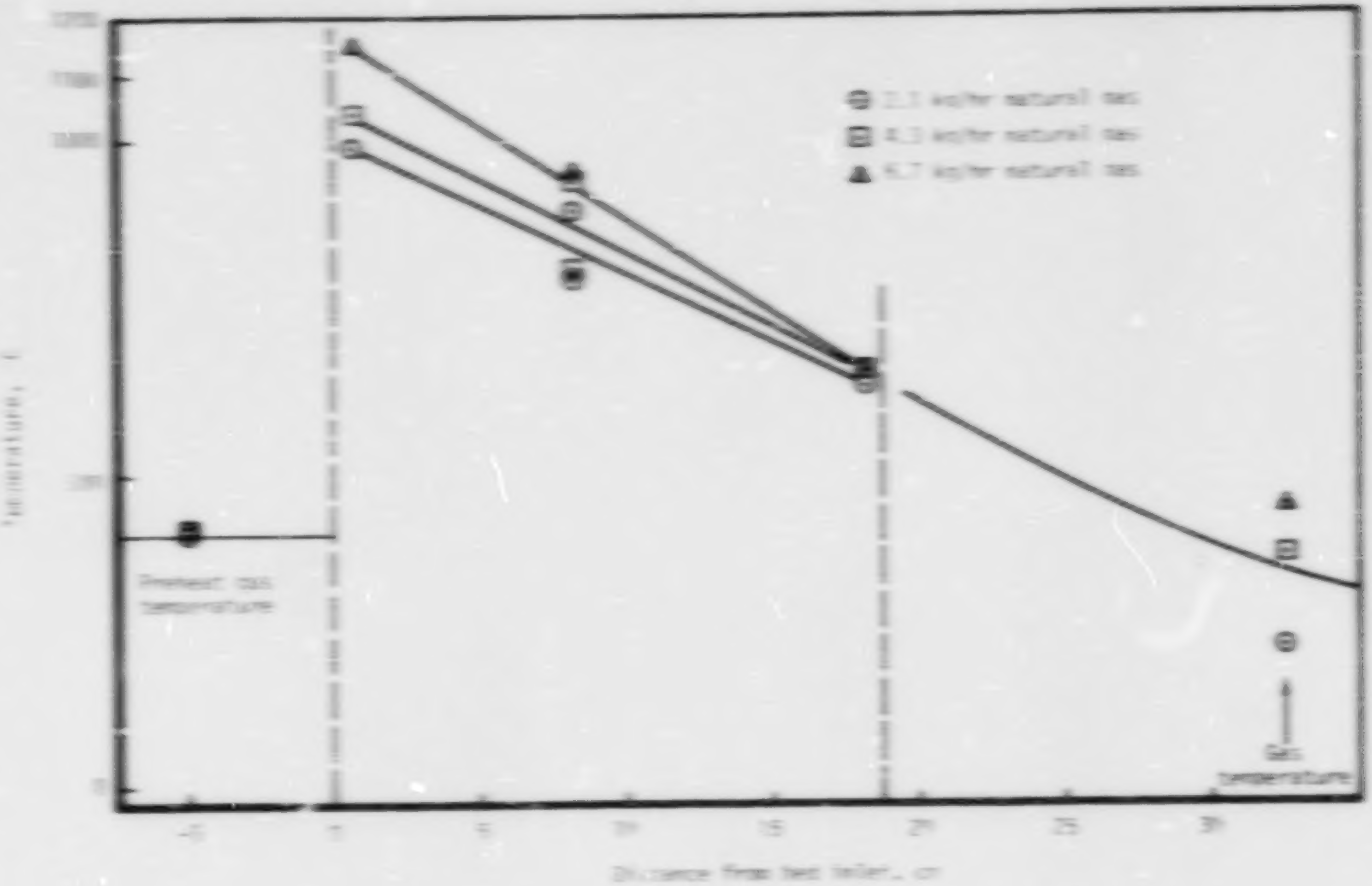

Figure 74. Bed temperature profiles at 100 percent TA vs. throughput.

STATUS OF FLUE GAS TREATMENT TECHNOLOGY FOR CONTROL OF NO_x AND SIMULTANEOUS CONTROL OF SO_x AND NO_x

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ABSTRACT

The status of flue gas treatment technology for control of NO_x and simultaneous control of NO_x and SO_x applicable to stationary combustion sources is presented. Dry processes and wet processes are described and applications discussed with respect to performance, operating experience, and economics.

As a result of a very stringent NO_x ambient standard in Japan, the Japanese NO_x flue gas treatment technology appears to be the most advanced in the world. For this reason, Japanese technology is emphasized in the paper. EPA's past, current, and planned flue gas treatment program is also discussed.

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INTRODUCTION

Nitrogen oxides (NO_x) in the atmosphere have been determined to have adverse effects on human health and welfare. To aid in preventing these adverse effects, the Industrial Environmental Research Laboratory at Research Triangle Park, N. C. (IERL-RTP) is leading the U.S. Environmental Protection Agency's (EPA) efforts to develop and demonstrate NO_x control technologies for stationary combustion sources. There are two main technologies being developed: combustion modification and flue gas treatment.

> Combustion modification (CM) technology attempts to minimize the formation of NO_x during the combustion process. CM techniques include staged combustion, low excess air operation, flue gas recirculation, water injection, and burner redesign. CM technology should be able to reduce NO_x emissions from stationary combustion sources by 50% or more in a relatively cost effective manner. CM technology will not be discussed in this paper; however, additional information is available from other sources.[1]
>
> Flue gas treatment (FGT) technology attempts to remove NO_x from the gaseous products of combustion. FGT techniques include dry selective catalytic reduction processes and wet scrubbing processes. FGT technology should be able to reduce NO_x emissions by 90% and has the potential for 90% control of both NO_x and SO_x emissions.

NO_x FGT research and development programs have received a relatively low level of funding by EPA since it has not been determined conclusively that high NO_x removal efficiencies will be required to achieve and maintain the current National Ambient Air Quality Standards (NAAQS). However, there are significant uncertainties which may affect the required level of NO_x control. Due to these uncertainties, EPA is proceeding with small scale NO_x FGT experimental projects in parallel with control strategy and technology assessment studies. One phase of the assessment is an evaluation of Japanese FGT technology which has progressed to the point of being commercially applied to gas- and oil-fired sources. In addition, the Japanese are developing processes for application to flue gas from coal-fired sources. EPA is investigating the Japanese and other worldwide technologies for potential application to the U.S. coal-fired situation to save both development time and money. Through these actions, the basic foundation will be established if the technology is required in the United States and acceleration of the development program becomes necessary.

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FLUE GAS TREATMENT PROCESSES

There are two main categories of flue gas treatment (FGT) processes for the control of NO_x and the simultaneous control of NO_x and SO_x emissions from stationary combustion sources: dry processes and wet processes. A description of the most promising processes in each category and their developmental status in Japan is discussed below.

DRY PROCESSES

The following dry process types are being developed:

Selective catalytic reduction
Selective noncatalytic reduction
Adsorption
Nonselective catalytic reduction
Catalytic decomposition
Electron beam radiation

Of these, only selective catalytic reduction (SCR) has achieved notable success in treating combustion flue gas for removal of NO_x and has progressed to the point of being commercially applied. The other process types are much less attractive at this time. Selective noncatalytic reduction processes do not achieve high NO_x removal efficiences and adsorption processes are not applicable to combustion sources. Nonselective catalytic reduction, catalytic decomposition, and electron beam radiation processes are at a very low level of development. These process types will not be discussed in this paper, but additional information is available from other sources.[2,3,4,5]

Dry NO_x Processes

Selective catalytic reduction processes are based on the preference of ammonia (NH_3) for NO_x over other flue gas constituents. Since the oxygen enhances the reduction, the reactions can best be expressed as:

$$4NH_3 + 4NO + O_2 \xrightarrow{\text{catalyst}} 4N_2 + 6H_2O \qquad (1)$$

$$4NH_3 + 2NO_2 + O_2 \xrightarrow{\text{catalyst}} 3N_2 + 6H_2O \qquad (2)$$

Reaction (1) predominates since approximately 90-95% of the NO_x in combustion flue gas is in the form of NO. Since 1 mole of NH_3 is required per mole of NO, most processes operate with an NH_3/NO mole ratio of 0.9 to 1.1. The reaction temperature is usually in the range of 300 to 450°C, but space velocities vary considerably depending on the process. Under these operating conditions, NO_x removal efficiencies of 90% or greater are typical.[4]

The catalysts used in SCR processes vary with process developer. However, there are some general traits known about the catalysts. The catalyst carrier or substrate is usually alumina, silica, or titanium dioxide. Alumina is satisfactory for application to flue gases without SO_x such as from natural gas firing. However, alumina tends to react with SO_x, particularly SO_3, to form aluminum sulfate. This "poisons" the catalyst by decreasing the available surface area and the catalyst activity. Titanium dioxide and silica are less susceptible to attack by SO_3 and are applicable to flue gas from heavy oil or coal firing. The active metal on the substrate may include Co, Cr, Cu, Fe, Mn, Ni, Pt, and V or combinations thereof, but the exact composition of the catalyst is usually proprietary. These metals or their oxides can also react with the SO_x to form sulfates. Many of these sulfates are also catalytic in the reduction of NO with NH_3, and therefore, can be tolerated. The catalysts are normally designed to have a life of at least 1 year.[4,5]

The formation of ammonium sulfate and bisulfate is a major concern with SCR processes. Ammonium bisulfate will form downstream of the reactor if NH_3 and SO_3 are present in sufficient quantities and if the gas temperature drops sufficiently. It is very difficult to avoid the conditions for formation; for example, ammonium bisulfate will form if the gas contains 10 ppm of NH_3 and 10 ppm of SO_3 at a temperature of 210°C. Ammonium sulfate will form at lower temperatures. Fine particulate emissions of these compounds are a concern, but the major problem with ammonium sulfate and bisulfate is deposition on heat exchanger surfaces. Since these compounds are very corrosive and interfere with heat transfer, the heat exchanger must be made of corrosion resistant material and must be cleaned periodically by soot blowing or water washing. Approaches to preventing this formation entail use of an ammonia decomposition catalyst or operation at lower NH_3/NO ratios.[4,5]

Another concern with SCR processes is catalyst plugging. Significant progress has been made in avoiding plugging problems through reactor and catalyst design. Fixed bed reactors, such as parallel passage, tube, and honeycomb, are being designed which can tolerate particle loadings typical of coal firing. Moving bed reactors are also being developed which can tolerate and remove moderate amounts of particles.[4,5] However, the particle concentrations acceptable to a moving bed reactor are approximately an order of magnitude less than those tolerated by a fixed bed system. The space velocity through a moving bed reactor is expected to be about double that of a fixed bed reactor, but the pressure drop across the moving bed reactor should be less.

Published information on the cost of SCR processes is limited and estimates available are based on different design premises. The reported estimates of the required capital investment range from \$10 to \$80/kW with an average of about \$30/kW. The revenue requirements range from 0.2 to 3.3 mills/kWh with an average of about 1.7 mills/kWh.[4,5]

A list of Japanese SCR process developers is given in Table I along with information on their developmental status. There are 16 commercial scale plants in operation treating 100,000 to 750,000 Nm^3/hr of flue gas (33 to 250 MW). In addition, there are 11 prototype plants treating from 15,000 to 99,499 Nm^3/hr of flue gas and numerous pilot and bench scale plants in operation.[6] The prototype and commercial scale plants are achieving 90% control of the NO_x from flue gas derived primarily from gas- and oil-fired sources. The operating experience in Japan qualifies NO_x control by SCR as a viable control technique in the U.S. when high NO_x removal efficiencies are required from gas- and oil-fired sources. SCR technology has not been demonstrated in Japan on coal-fired sources although several of the pilot plants are currently evaluating such an application and larger scale demonstrations are expected in the near future. In fact, a northern utility in Japan is considering installation of a 90 MW SCR system on a coal-fired boiler which will begin operation in 1980.[6]

Dry Simultaneous NO_x/SO_x Processes

There are two noteworthy variations of SCR processes which have the capability to simultaneously remove NO_x and SO_x: the activated carbon process and the Shell copper oxide process.

The activated carbon process requires a special carbon bed which acts as an adsorbent for SO_x and as a catalyst in the reduction of NO_x with NH_3. When the bed is saturated with SO_x, flue gas is switched to a fresh bed, the carbon is regenerated, and a concentrated SO_2 stream is produced which can be used to generate a salable byproduct. The process has the potential for removing 90% of both pollutants, but its application may be limited to flue gas containing relatively equal concentrations of NO_x and SO_x.[5] The economic projections for the process are about $65/kW for the capital investment and 6.3 mills/kWh in revenue requirements. The activated carbon process is being evaluated on a pilot plant scale in Japan by Takeda, Unitika, and Sumitomo Heavy Industries.[5]

In the Shell process, copper oxide reacts with SO_2 to form copper sulfate. The copper sulfate and, to a lesser extent, the copper oxide act as catalysts in the reduction of NO_x with NH_3. As in the activated carbon process, a multiple bed system is required so that a bed is available for acceptance while regeneration takes place. In the regeneration cycle, hydrogen is used to reduce the copper sulfate and a concentrated SO_2 stream is produced which can be used to generate a salable byproduct.[6] The economic projections for the process are $131/kW for the capital investment and 5 mills/kWh for the revenue requirements.[5] The process has been installed at the Showa Yokkaichi Sekiyu Company (SYS) plant in Yokkaichi, Japan on a commercial scale (120,000 Nm^3/hr) and has removed 90% of the SO_x and 70% of the NO_x.[5]

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WET PROCESSES

The following wet process types are being developed:

Oxidation-Absorption Processes
Absorption-Oxidation Processes
Oxidation-Absorption-Reduction Processes
Absorption-Reduction Processes

Wet NO_x Processes

The first two process types are generally for NO_x control only. In oxidation-absorption processes, the relatively insoluble NO is oxidized in the gas phase to NO_2 which is absorbed into the liquid phase. The typical oxidizing agents used are ozone and chlorine dioxide. The absorbents vary with process developer. The process seems more feasible for flue gas containing equimolar mixtures of NO and NO_2 which is not typical of combustion flue gas. Much of the absorbed NO_2 remains in the liquid phase in the form of nitrate salts which are water pollutants.[6]

In absorption-oxidation processes, NO is absorbed directly into the liquid phase and then oxidized. Liquid oxidizing agents such as sodium hypochlorite or hydrogen peroxide are used to convert the NO to a nitrate salt. Due to the insolubility of NO, relatively large absorbers are required. In addition, the process is not applicable to flue gas containing SO_2 since the more soluble SO_2 would consume the liquid oxidizing agent by converting the absorbed sulfite ion into sulfate.[6]

Due to their complexity, limited applicability, and water pollution problems, wet processes cannot compete economically with dry selective catalytic reduction processes for control of NO_x in combustion flue gas. Therefore, these process types will not be addressed further in this paper, but additional information is available from other sources.[2,3,4,5]

Wet Simultaneous NO_x/SO_x Processes

The attractiveness of wet processes is their potential for simultaneous removal of NO_x and SO_x. Oxidation-absorption-reduction processes and absorption-reduction processes are designed for this type of control.

The oxidation-absorption-reduction processes basically evolved from flue gas desulfurization (FGD) systems. A gas phase oxidant is injected before the scrubber to convert NO to the more soluble NO_2. The NO_2 is then absorbed into an aqueous solution with SO_2. The absorbent varies with the type of [illegible] system being modified. The absorbed SO_2 forms a sulfite ion which reduces a portion of the absorbed nitrogen oxides to molecular nitrogen. The [illegible] nitrogen oxides are removed from the waste water as nitrate salts. The remaining sulfite ions are oxidized into sulfate by air and removed as gypsum. The percentage of nitrogen oxides going either to the preferred molecular nitrogen or to the troublesome nitrate salts is uncertain; however, it is estimated to be about 50-50, but this can vary considerably.[6]

The oxidation-absorption-reduction processes have the potential to remove 90% of both SO_x and NO_x from combustion flue gas.[4] However, there are several drawbacks remaining to be overcome before the processes can be widely applied. The process chemistry is complex and use of a gas phase oxidant, such as ozone or chlorine dioxide, is expensive. Chlorine dioxide, although cheaper than ozone, adds to the waste water problems created by the nitrate salts. Chlorine dioxide also causes concern due to the possibility for chlorination of organics in the waste water to produce carcinogenic compounds.

Despite these drawbacks, the potential of a simultaneous removal process warrants further research and development. Table II lists the process developers evaluating oxidation-absorption-reduction technology. One small commercial scale plant (11 MW), three prototype, and three pilot plants are currently being operated in Japan.[6] As with SCR processes, published economic data are limited, but the average reported capital investment is about $110/kW and the average revenue requirement is about 7.5 mills/kWh.[5]

The absorption-reduction processes were seemingly developed to avoid the use of a gas phase oxidant. A chelating compound, such as ferrous-EDTA (ethylenediamine tetraacetic acid) which has an affinity for the relatively insoluble NO, is added to the scrubbing solution. The NO is absorbed into a complex with the ferrous ion and the SO_2 is absorbed as the sulfite ion. The NO complex is reduced to molecular nitrogen by reaction with the sulfite ion. A regeneration step recovers the ferrous chelating compound and oxidizes the sulfite ion into sulfate which is removed as gypsum.[5]

The absorption-reduction processes also have the potential to remove 90% of both the NO_x and SO_x in combustion flue gas.[4] Although the processes seem to have advantages over the oxidation-absorption-reduction processes, there are obstacles to be overcome before the processes can be widely applied. Even with the addition of the chelating compounds, a large absorber is required to absorb the NO. The replacement, recovery, and regeneration costs of the chelating compounds, although potentially less than the gas phase oxidants, are still significant. The process chemistry is complex and is sensitive to the flue gas composition of SO_2, NO_x, and oxygen. The molar ratio of SO_2 to NO_x must remain above approximately 2.5 and the oxygen concentration must remain low.[5]

Table II also lists the process developers evaluating absorption-reduction technology in Japan. There are four pilot or bench scale plants currently being operated.[6] The average reported capital investment is about $96/kW and the revenue requirements are about 6.3 mills/kWh.[5]

Table III summarizes the status, cost, and performance of the dry and wet processes for control of NO_x and simultaneous control of NO_x and SO_x.

CONTROL OF NO_x, SO_x, AND PARTICLES

Over 90% control of NO_x, SO_x, and particles may eventually be required in the U.S. for stationary combustion sources, especially for new, large, coal-fired sources. Schematics of some of the alternatives for such an overall control system are shown in Figure 1.

Perhaps the ideal situation would be represented by one control device that simultaneously removes NO_x, SO_x, and particles. Such a control device is not yet available, but it is conceivable that a wet scrubber system could remove all three pollutants. Such a system is represented in Schematic A of Figure 1. Since the recovery of heat from the flue gas is important, a heat exchanger is shown in the schematic. A reheater is also shown since most wet scrubber systems require reheat of the flue gas prior to its discharge from the stack.

The most developed overall control system is NO_x control by selective catalytic reduction (SCR), SO_x control by flue gas desulfurization (FGD), and particle control by an electrostatic precipitator (ESP). The sequence of these control devices is variable as illustrated in Schematics B, C, and D. Schematic B shows particle control first, followed by NO_x control, and then SO_x control. In this configuration, the SCR system could be a moving bed type which would require most of the particles to be removed first. To maintain high temperatures needed by the SCR system, a hot-ESP would be necessary. The requirement for a hot-ESP could be avoided by use of a fixed bed SCR system which could tolerate high particle concentrations. This configuration is illustrated in Schematic C.

Since the sulfur compounds in the flue gas lower the resistivity of the fly ash and improve the collection efficiency of the ESP, it is not deemed advantageous to have the ESP follow the FGD system. However, it is uncertain if ammonia, ammonium sulfate, or ammonium bisulfate will leave the SCR system and adversely affect the performance of the FGD system. To avoid this possibility, the SCR system could follow the FGD system as shown in Schematic D. However, the disadvantage of this configuration is the extensive reheat that would be required to raise the flue gas temperature to a level suitable for the SCR system.

The simultaneous NO_x/SO_x systems present an apparent simplification of the control system as shown in Schematics E, F, and G of Figure 1.

Schematic E depicts the activated carbon process and Schematic F illustrates the Shell process for dry simultaneous NO_x/SO_x control. Two configurations are presented due to the different tolerance of particle concentrations and to the different operating temperatures of the processes. The wet simultaneous NO_x/SO_x control systems are shown in Schematic G and can be represented by either the oxidation-absorption-reduction processes or by the absorption-reduction processes.

At this time it is mere speculation as to which configuration will emerge as the optimum overall control system from a technical and economic standpoint. In all probability, the optimum system will be dependent on specific flue gas and site considerations as well as user preference.

EPA'S NO_x FLUE GAS TREATMENT PROGRAM

High NO_x removal efficiencies may not be required to achieve and maintain the current National Ambient Air Quality Standards (NAAQS). Further, the current New Source Performance Standards (NSPS) for NO_x can be achieved by implementation of combustion modification techniques which are more economical than FGT processes. However, there are significant factors which may cause the NAAQS and the NSPS to become more stringent. These include: the alarming increase in NO_x emissions from stationary combustion sources projected for the next decade, the possibility of a short-term NO_2 NAAQS, the relationship of NO_x emissions to levels of photochemical oxidants, the impact of increased use of coal resources, the impact of relaxing mobile source emission standards, the role of NO_x emissions as precursors to other pollutants of concern such as PAN (peroxyacyl nitrates), other nitrates, nitrosamines, and nitric acid, and the health effects of NO_x and related pollutants.

If more stringent standards are promulgated, then NO_x FGT technology may be required to meet the standards to protect human health and welfare. Therefore, the NO_x FGT program is proceeding with experimental projects progressing toward full scale demonstration of highly efficient NO_x and simultaneous NO_x/SO_x control technology in parallel with control strategy and technology assessment studies. The results of these studies will assist in determining the appropriate scale of the experimental projects. EPA's past, current, and planned activities in these areas are summarized below.

CONTROL STRATEGY AND TECHNOLOGY ASSESSMENT STUDIES

The control strategy and technology assessment studies are mainly research projects to examine various aspects of NO_x control technology and to determine if and when NO_x FGT technology will be needed in the U.S.

Assessment of Japanese Technology

Since Japanese technology in this field is more advanced than any other country's, EPA has sponsored the publication of periodic reports and papers to facilitate the transfer of information on NO_x and NO_x/SO_x abatement technology from Japan. These documents have been mainly prepared by Dr. Jumpei Ando of Chuo University in Tokyo, Japan.[2,3,4,7,8] Dr. Ando is also assisting EPA in activities associated with the Stationary Source Pollution Control Project of the US/Japan Environmental Agreement which includes a subproject on NO_x and NO_x/SO_x FGT technology.

In addition to monitoring published information from Japanese sources, EPA personnel have made periodic trips to Japan to observe testing facilities and to discuss the technology with process developers and operating personnel. The most recent trip was in March 1977.

Ozone Oxidation of NO[9]

Gas phase oxidation of NO to NO_2 is essential for wet oxidation-absorption-reduction processes. Therefore, a task order was issued by IERL-RTP to the Research Triangle Institute to analyze the supply, demand, production economics, and energy consumption of this key FGT process step. The results of the study indicate that only a stoichiometric amount of ozone is required to achieve essentially complete conversion of NO to NO_2 which may be subsequently scrubbed from the gas stream.

The energy requirements and the capital and operating costs were examined for ozone generation with both air and oxygen as input to the ozone generator. Approximately 13% more energy is required for ozone generation from oxygen than from air. The capital investment for ozone generation from oxygen is about 3 times as large as that required from air, and operating costs are about twice as large. For a 500 MW plant with air as input to the ozone generator, the estimates for oxidizing 200 ppm of NO were: energy requirement, 1.1×10^8 kWh/yr or 3.1% of station capacity; capital investment, \$17.60/kW; and operating costs, 2.0 mills/kWh. The 500 ppm concentration is representative of a coal-fired source with combustion modification techniques applied or an oil-fired source without supplementary NO_x control applied. The estimates are for oxidation of NO only; the energy requirements and cost of control for NO_2 would be additive.

The report indicates that unless there is a significant improvement in ozone generation technology, wet processes using ozone for oxidation of NO to NO_2 will be very expensive. However, since these processes have potential for simultaneous NO_x/SO_x control, the energy and cost impacts may be more acceptable.

NO_x Control Strategy Assessment

IERL-RTP contracted with Radian Corporation to determine the potential effectiveness of applying NO_x controls to large stationary combustion sources. The Chicago Air Quality Control Region (AQCR) was selected for a modeling study of emissions from point, area, and mobile sources to determine the relative impact of each category on ambient NO_x concentrations. The calibrated dispersion model predictions of annual average concentrations indicate that the major point sources, which contributed nearly 60% of the total NO_x emissions in Chicago, accounted for less than 10% of the ambient NO_2 levels in 1974. Preliminary investigation of expected short-term concentrations of total NO_x shows that major point sources may contribute as much as 80% of measured NO_x levels. Therefore, it appears that stringent NO_x control for large point sources may be required to meet a potential short-term NO_2 standard, but cannot be justified currently on the basis of the existing annual average NO_2 standard.[10] However, NO_x emissions from stationary combustion sources are expected to increase significantly in the next decade.

As a result of these findings, the Chicago AQCR modeling study was expanded to determine more accurately the short-term ambient NO_2 levels, to project the annual and short-term NO_2 concentrations to 1985, and to assess the use of NO_x emission control on stationary combustion sources to attain or maintain compliance with possible NO_2 ambient short-term and annual average standards. The results of this study should be available by early 1978.

Another Radian Corporation study is seeking to determine the key factors relating to "if" and "when" NO_x FGT technology will be needed in the U.S. Since research and development of a technology should lead its application by several years, it is necessary to monitor factors which could require implementation of NO_x FGT technology in the near future. By these efforts, the decision to emphasize, maintain, or terminate the research, development, and demonstration of NO_x FGT technology can be made on the best available information. This study should also be available in early 1978.

Economic Assessments of NO_x FGT Processes

The Tennessee Valley Authority (TVA), through an interagency agreement with EPA, is developing comparative economics of NO_x and NO_x/SO_x FGT emission control processes. This state-of-the-art review will be conducted in two phases. Phase I will evaluate and summarize the technical feasibility of all candidate NO_x control processes being offered in the U.S. and Japan. The Phase I report, which includes descriptions of about 45 processes, should be published in the summer of 1977.[5] Phase II will concentrate on the most promising processes identified in Phase I and will perform a preliminary economic assessment of each, including development of material and energy balances. In addition, a direct comparison of the economic and technical feasibility of the dry and wet processes will be made to determine the most effective method to remove NO_x and SO_x from combustion flue gas. The project is cofunded by IERL-RTP and the Electric Power Research Institute.

EPA is planning a third phase of the project to prepare detailed economic projections of as many as four of the most promising processes. This activity should be complete in late 1978. Further, it is contemplated that a study will be conducted during this phase to determine the impact of ammonia utilization by SCR processes. The cost and energy requirements of ammonia generation for a typical utility application will be examined. In addition, the impact on the supply, demand, and cost of ammonia worldwide will be analyzed. This study may be available by the end of 1977.

EXPERIMENTAL PROJECTS

EPA's experimental projects have been directed toward enhancing the evolution of FGT technology from bench scale research to full scale demonstration on coal-fired sources by the mid-1980's. The technology must be applicable to utility and large industrial combustion sources and must achieve highly efficient NO_x and simultaneous NO_x/SO_x control in a relatively energy efficient and economical manner.

Bench Scale Catalyst Research[11]

In 1975, a research grant was awarded to the University of California at Los Angeles (UCLA), School of Engineering and Applied Sciences to further the development of promising catalysts. The study extended the catalyst screening work performed earlier by UCLA under an IERL-RTP contract with TRW, Inc.[12] The objectives of the grant were to optimize the compositions of vanadium and iron-chromium catalysts for selective reduction of NO_x with ammonia and to perform long-term durability studies of the optimum catalyst compositions in flue gas containing sulfur dioxide. The results of the study, completed in mid-1976, indicated that a 15% loading of vanadium oxide on alumina support material and a 10% loading of iron oxide-chromium oxide on alumina support material with an iron/chromium ratio of 9:1 were the optimum catalyst formulations.

Parametric tests showed that both catalysts were selective, in that only the NO_x was reduced. The tests also showed strong enchancement of NO_x conversion rates due to the presence of O_2 under typical operating conditions. CO_2, H_2O, and SO_2 did not affect the NO_x reduction in the concentration ranges applicable to power plant exhaust. Both catalysts were most active between 400°C and 425°C and required excess NH_3 for maximum activity. Long-term durability tests of both catalysts in the presence of SO_x indicated no degradation in catalyst performance. Typical conversion levels for the vanadium and iron-chromium catalysts operating at 400°C in simulated flue gas were about 90% and 80%, respectively, at 20,000 hr^{-1} space velocity. In addition, preliminary tests of iron-vanadium and iron-chromium-vanadium catalysts indicated 90% removal of NO_x from the simulated flue gas.

Pilot Plant Evaluation of Gas and Oil Firing[13]

In 1973, a contract was awarded to Environics, Inc. to evaluate the performance, reliability, and practicality of a SCR system with ammonia and a platinum catalyst on alumina support material. A pilot plant, treating a slipstream from an operating utility boiler, was designed, installed, and tested on gas and oil firing. Laboratory testing was conducted to supplement the pilot plant testing. Satisfactory results were found on gas-fired operation with 85-90% NO_x removal achieved for over 4000 hrs at a space velocity of 50,000 hr^{-1}. Results on oil-fired operation indicate that the catalyst system was not suitable for flue gas containing SO_x. The maximum NO_x removal efficiency achieved was 65% with the average only 50%. Fluctuation in flue gas temperature and catalyst plugging with soot and ammonium sulfate caused problems on oil-fired operation.

Pilot Plant Evaluation on Coal Firing

The next phase of the experimental program is evaluation of FGT processes on a coal-fired application. A request for proposal was issued in September 1976, and best and final offers are currently being evaluated. Contract award is anticipated by the end of September 1977. It is contemplated that two contracts will result from this procurement process. One will be for a pilot plant to evaluate removal of NO_x emissions, and the other will be to evaluate simultaneous removal of NO_x and SO_x. However, budgetary constraints and technical considerations may impact on the final decision in this regard.

The pilot plants must treat a flue gas volume equivalent to 0.5 MW and achieve a NO_x removal efficiency of 90%. For the simultaneous control of NO_x and SO_x, 90% removal of both pollutants must be achieved. The pilot plant projects will each consist of a 24 month program which will be conducted in four phases. Phase I includes the preparation of a detailed process design and an estimation of capital and operating costs for the pilot plant. Following erection of the pilot plant and mechanical acceptance testing in Phase II, the contractor will perform system start-up and debugging, parametric testing, and optimization testing over a wide range of flue gas conditions during Phase III. Phase IV provides for testing and evaluation of the plant during 90 days of continuous operation. It is currently anticipated that final reports will be published on the results of the pilot plant operations in early 1980. A project manual conveying the total concept of the proposed plant is planned for early 1978. In addition to these projects, there is the possibility of a pilot plant project being initiated in 1977 with the Tennessee Valley Authority.

The pilot plant projects will enable an assessment of the technical, environmental, energy, and economic aspects of applying NO_x and NO_x/SO_x FGT technology to the U.S. coal-fired situation. This information, in conjunction with the control strategy and technology assessment studies, will provide technical and budgetary direction and emphasis for EPA's NO_x and NO_x/SO_x FGT program.

TABLE 1. MAJOR NO_x SELECTIVE CATALYTIC REDUCTION PLANTS IN JAPAN[5]

Process Developer	Plant Owner	Plant Site	Capacity (Nm^3/hr)	 (MW) Approx.	Source of Gas	Start-up
Asahi Glass	Asahi Glass	Keihin	70,000	23.3	Glass Furnace	Apr. 1976
Hitachi Ltd.	Kawasaki Steel	Chiba	350,000	116.6	Coke Oven	Oct. 1976
Hitachi Ltd.-Mitsubishi PC	Mitsubishi PC	Yokkaichi	150,000	50.0	Oil-Fired Boiler	Dec. 1975
Hitachi Zosen	Toshin Steel	Himeji	70,900*	23.6	Heating Furnace	June 1976
Hitachi Zosen	Kawasaki Steel	Chiba	750,000	250.0	Sintering Machine	Nov. 1976
Japan Gasoline	Kashima Oil	Kashima	50,000	16.6	Heating Furnace	Nov. 1975
Japan Gasoline	Fuji Oil	Sodegaura	70,000	23.3	CO Boiler	Mar. 1976
Mitsubishi H.I.	Fuji Oil	Chiba	200,000	66.6	Oil-Fired Boiler	Late 1977
Mitsui S.B.-Mitsui P.C.	Mitsui Pet. Chem.	Chiba	200,000	66.6	Oil-Fired Boiler	Sep. 1975
Mitsui S.B.-Mitsui P.C.	Ukishima Pet. Chem.	Chiba	240,000	80.0	Oil-Fired Boiler	Aug. 1976
Mitsui Toatsu	Mitsui Toatsu	Takaishi	170,000*	56.6	Ammonia Plant	Oct. 1976
Mitsui Toatsu	Mitsui Toatsu	Takaishi	87,000*	38.6	Ammonia Plant	Mar. 1976
Mitsui Toatsu	Osaka Pet. Chem.	Takaishi	90,900*	30.3	Heating Furnace	Sep. 1976
NKK-Sentetsu	Nippon Yakin	Kawasaki	15,000	5.0	Oil-Fired Boiler	June 1976
Osaka Gas	Osaka Gas	Sakai	63,900*	21.3	Gas Generator	July 1976
Seitetsu Kagaku	Seitetsu Kagaku	Kakogawa	15,040	5.0	Oil-Fired Boiler	June 1975
Sumitomo Chemical	Sumitomo Chem.	Sodegaura	30,000	10.0	Oil-Fired Boiler	July 1973
Sumitomo Chemical	Sumitomo Chem.	Anegasaki	100,000*	33.3	Gas-Fired Boiler	Feb. 1975
Sumitomo Chemical	Higashi Nihon Met.	Sodegaura	200,000*	66.6	Heating Furnace	May 1974
Sumitomo Chemical	Sumitomo Chem.	Anegasaki	200,000*	66.6	Gas-Fired Boiler	Feb. 1975
Sumitomo Chemical	Sumitomo Chem.	Niihama	200,000*	66.6	Heating Furnace	Mar. 1975
Sumitomo Chemical	Nihon Ammonia	Sodegaura	250,000*	83.3	Heating Furnace	Mar. 1975
Sumitomo Chemical	Sumitomo Chem.	Sodegaura	250,000	83.3	Oil-Fired Boiler	Mar. 1976
Sumitomo Chemical	Sumitomo Chem.	Sodegaura	300,000	100.0	Oil-Fired Boiler	Oct. 1976

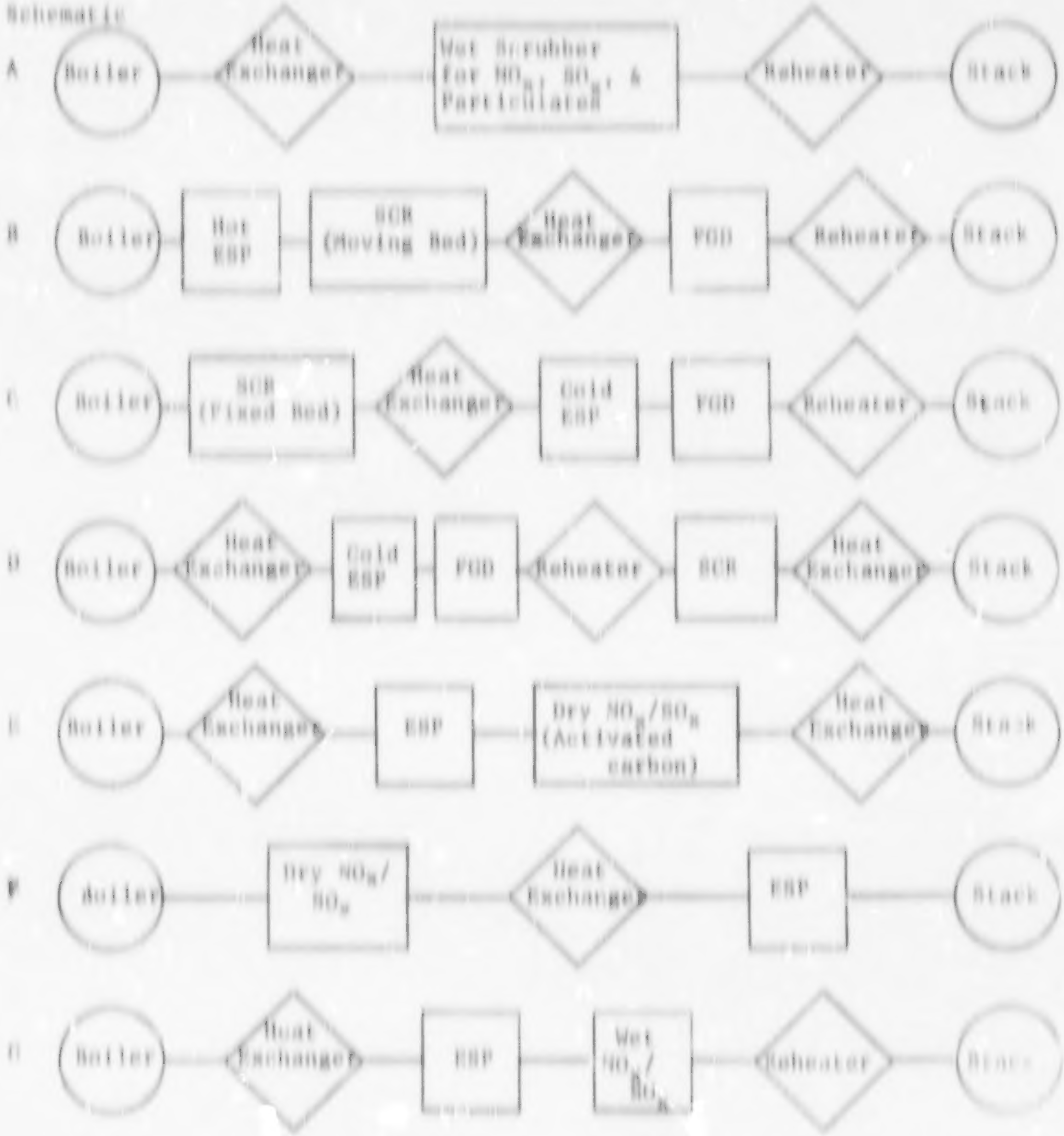
*Flue gas contains minimum amounts of SO_x and particles

TABLE 11. MAJOR WET NO_x/SO_x CONTROL PLANTS IN JAPAN[a]

Process Developer	Plant Owner	Plant Site	Capacity (Nm³/hr)	Capacity (MW) Approx.	Source of Gas	Start-up
OXIDATION - ABSORPTION - REDUCTION PROCESSES						
Chiyoda	Chiyoda	Kawasaki	1,000	0.3	Oil-Fired Boiler	Aug. 1973
Ishikawajima H.I.	Ishikawajima H.I.	Yokohama	5,000	1.6	Oil-Fired Boiler	Sep. 1975
Mitsubishi H.I.	Mitsubishi H.I.	Hiroshima	2,000	0.6	Oil-Fired Boiler	Dec. 1974
Osaka Soda	Osaka Soda	Amagasaki	60,000	20.0	Oil-Fired Boiler	Mar. 1976
Shirogane	Mitsui Sugar	Kawasaki	48,240	16.0	Oil-Fired Boiler	Aug. 1974
Sumitomo Metal-Fujikasui	Sumitomo Metal	Amagasaki	62,000	20.6	Oil-Fired Boiler	Dec. 1973
Sumitomo Metal-Fujikasui	Toshin Steel	Fuji	100,000	33.3	Heating Furnace	Dec. 1974
Sumitomo Metal-Fujikasui	Sumitomo Metal	Osaka	39,000	13.0	Oil-Fired Boiler	Dec. 1974
ABSORPTION - REDUCTION PROCESSES						
Asahi Chemical	Asahi Chemical	Mizushima	600	0.2	Oil-Fired Boiler	Apr. 1974
Chisso Corp.	Chisso P.C.	Goi	300	0.1	Oil-Fired Boiler	Apr. 1974
Kureha Chemical	Kureha Chemical	Nishiki	5,000	1.6	Oil-Fired Boiler	Apr. 1975
Mitsui S.B.	Mitsui P.C.	Chiba	150	0.05	Oil-Fired Boiler	Apr. 1974

TABLE III. STATUS OF FLUE GAS TREATMENT PROCESSES

Process Type	Developmental Plants	Removal Efficiency (%) NO_x	SO_x	Approx. Capital Cost ($/kW)	Approx. Revenue Requirements (mills/kWh)
Dry Selective Catalytic Reduction (with ammonia)	16 commercial 11 prototype	≥ 90	N.A.	30	2.7
Dry Simultaneous NO_x/SO_x					
Activated carbon	3 pilot	~ 90	~ 90	65	6.3
Shell Copper Oxide	1 commercial	70	90	131	5.0
Wet Simultaneous NO_x/SO_x					
Oxidation-absorption-reduction	1 commercial 3 prototype 3 pilot	≤ 90	≥ 90	110	7.5
Absorption-reduction	4 pilot or bench	≤ 90	≥ 90	96	6.3


Schematic
A
Boiler
Heat Exchanger
Wet Scrubber for NO_x, SO_x, & Particulates
Reheater
Stack
B
Boiler
Hot ESP
SCR (Moving Bed)
Heat Exchanger
FGD
Reheater
Stack
C
Boiler
SCR (Fixed Bed)
Heat Exchanger
Cold ESP
FGD
Reheater
Stack
D
Boiler
Heat Exchanger
Cold ESP
FGD
Reheater
SCR
Heat Exchanger
Stack
E
Boiler
Heat Exchanger
ESP
Dry NO_x/SO_x (Activated carbon)
Heat Exchanger
Stack
F
Boiler
Dry NO_x/ SO_x
Heat Exchanger
ESP
Stack
G
Boiler
Heat Exchanger
ESP
Wet NO_x/ SO_x
Reheater
Stack

ESP = Electrostatic Precipitator for Particle Control
FGD = Flue Gas Desulfurization for SO_2 Control
SCR = Selective Catalytic Reduction for NO_x Control

FIGURE 1 - POTENTIAL EQUIPMENT CONFIGURATION FOR NO_x, SO_x, AND PARTICLE CONTROL

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EVALUATION OF COMBUSTOR DESIGN CONCEPTS APPLICABLE TO ADVANCED LOW-Btu GAS FIRED SYSTEMS

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This paper was not received in time for publication, and therefore will be inlcuded in Volume V.

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EVALUATION OF A PROTOTYPE SURFACE COMBUSTION FURNACE

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ABSTRACT

Evaluation of a Prototype Surface Combustion Furnace

by G. Blair Martin

The emissions characteristics of a prototype surface combustion residential furnace have been evaluated using both propane and natural gas. The combustion of premixed fuel and air takes place on a refractory surface without a visible flame. Heat is transferred from the surface to an air cooled firebox wall by radiation. This maintains a relatively low surface temperature and reduces the oxides of nitrogen (NO_x).

The furnace was operated over a range of excess air from 5 to 45% and with heat input from 16,000 to 24,000 watts. For a nominal operating point for natural gas at 10% excess air, NO_x emissions were less than 15 ppm (as measured). CO and HC emissions were also low. Furnace efficiency calculated from flue losses was greater than 80%. Performance on propane was similar.

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INTRODUCTION

The Combustion Research Branch (CRB) of the EPA's Industrial Environmental Research Laboratory at Research Triangle Park, N.C., has the responsibility for carrying out a combustion modification R&D program directed toward control of nitrogen oxides and other pollutants from stationary combustion sources. In addition to pollutant emission control it appears that the technology can also lead to equal or improved efficiency of energy utilization compared to current practice. The majority of the R&D is carried out under EPA contracts initiated and directed by CRB and performed by private organizations. However, CRB also maintains an in-house research program in a number of areas. This in-house activity provides direct project officer expertise in combustion research and provides the capability for initial evaluation of potential control techniques or promising novel concepts applicable to combustion systems. The results of many of these studies are well documented.

A continuing activity is the evaluation of novel combustion devices which may have the potential for very low pollutant emissions. One such device is a prototype of a residential gas fired furnace using surface combustion to promote fuel oxidation. The purpose of this paper is to describe the performance of that prototype.

BACKGROUND

Stationary combustion equipment used in residential heating can be classified as area sources. Pollutant emissions from an individual unit are

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relatively small, the discharge into the atmosphere is near ground level in populated areas, the emissions are concentrated in the heating season and the number of sources is large (i.e., about 55×10^6 units). Although the residential sources contribute only about 3% of the mass emissions of nitrogen oxides (NO_x), the environmental impact may be much more significant. In addition, these sources require relatively clean fuels (e.g., natural gas and distillate oil) and account for over 10% of the stationary source energy usage (ref. 1). In 1974, residential warm air furnaces used over 4.5×10^{12} kJ of fuel with natural gas and propane providing about 60% and fuel oil providing the balance. Based on these factors, it appears that both emission control and energy conservation in this source class is required. The emission levels for distillate oil fired residential furnaces have been characterized (ref. 2) and there has been some technology development for reducing emissions and increasing efficiencies (ref. 3). Much less work has been done on gas fired residential furnaces because of less flexibility in adjusting operating conditions and relatively simpler equipment design. The normal residential gas furnace does not have a "burner" as such, but rather relies on natural draft to provide combustion air and to accomplish fuel and air mixing. The available gas pressure is used to entrain some air and to form a primary air and fuel mixture that is admitted to the combustion chamber through one or more log manifolds. Secondary air to complete combustion is admitted to the combustion chamber around the manifolds. Although the primary air can be controlled to a degree, there is essentially no way to control secondary air. Therefore, the overall excess air cannot be controlled to a significant degree.

The available emission data on gas fired furnaces are very limited. Hall (ref. 3) reported data for three gas furnaces with NO_x emissions ranging from 0.084 to 0.115 gm of NO_x (as NO) per 10^6 cal [i.e., 0.32 to 0.42 kg NO_x (as NO_2) per 10^{10} J]. Any given furnace could only be operated over a narrow range of excess air; however, the three different designs operated at levels in the range of 20 to 60% excess air. The emissions of carbon monoxide (CO) and hydrocarbon (HC) were low for all three furnaces at the normal operating point. DeWerth (ref. 4) measured emissions from

38 forced warm air gas furnaces in the AGA laboratory and reports an average NO_x value of 0.097 lbs NO_x (as NO_2) per 10^6 Btu [i.e., 0.415 kg NO_x (as NO_2) per 10^{10} J] with a small effect of furnace design. Decreasing the primary air setting to the point of yellow flame operation decreased the NO_x level by about 10%; however, CO emissions increased by a factor of 20 and the NO_2 component increased from about 5% of the total NO_x to the range of 10 to 17%. Data for other gas appliances and for modified furnace design also showed high fractions of NO_2 associated with higher CO levels. Several modifications of furnace design were examined with the most successful one achieving 37 ppm of NO_x [i.e., 0.172 kg NO_x (as NO_2) per 10^{10} J] at low CO levels by putting a screen in the flame zone to increase radiant heat transfer. Finally, Brookman (ref. 5) performed field measurements on 50 residential gas fired furnaces and boilers and reported average NO_x emissions of 112 lbs (as NO_2) per 10^6 ft^3 of gas [i.e., about 0.455 kg NO_x (as NO_2) per 10^{10} J].

The efficiency of the furnace is dependent on the extent of heat loss from the system by various avenues. The predominant energy losses are the following:

1. Latent heat of vaporization of the water formed during combustion which cannot be recovered without a condensing heat exchanger. About 10% of the gross heat input of natural gas is irretrievably lost in this form using current technology.

2. Sensible heat in the combustion products which is dependent on the amount of excess air used for combustion, the amount of dilution air and the temperature of the gas in the flue. This loss can be reduced by low excess air operation, elimination of dilution air and/or reduction of stack temperature.

3. Draft losses, which remove residual heat from the firebox during the off-cycle. This loss can be reduced by minimizing or eliminating air flow through the furnace during off-cycle.

4. Miscellaneous casing losses. These losses are normally held to a minimum by proper insulation of the furnace enclosure.

The significant features of these losses are discussed for fuel oil in reference 3. The general discussion also holds for natural gas, although differences in latent heat losses and system design will change the quantitative levels. DeWerth (ref. 4) reported that the average of furnaces tested in the AGA Lab had 5.8% CO_2 in the flue products (approximately 100% excess air); however, no flue temperatures were given. Flue losses for two units tested were reported to be 20.1 and 26.6%, based on steady state operation. The cycle average efficiency will be further reduced by the draft and casing losses.

EXPERIMENTAL APPROACH

This section provides information on several aspects of the experimental approach including: 1) the fuel supply system; 2) the Bratko prototype furnace; 3) the analytical instrumentation; and 4) the range of variables examined.

Fuel Supply

Natural gas was provided from a laboratory gas line at a pressure of 3.45×10^4 pascal gage (5 psig). Propane was provided from a pressurized gas bottle and the line pressure was controlled at 4.83×10^4 pascal gage (7 psig). The gas supply was passed through a dry gas meter to obtain a volumetric flow rate. Following this the pressure was regulated to 3.45×10^3 pascal gage (0.5 psig) and the gas passed through an ASTM orifice meter. The pressure drop across the orifice was used to adjust the gas flow to a constant value during a test series. The gas supply was connected to the fuel inlet system of the furnace.

Bratko Prototype Furnace

The furnace tested was a prototype of a surface combustion concept for use in residential gas furnaces. The concept is based on combustion of premixed fuel and air on the surface of a refractory matrix without visible flame. The glowing refractory surface radiates to a surrounding air cooled combustion chamber and, thereby, maintains the surface temperature at a relatively low value (i.e., below about 1250 K). A schematic of the surface combustor and firebox is shown in Figure 1. The combustion chamber was enclosed in a conventional upright furnace body and used a three speed circulating air fan to pass air over the heat exchange surface. The speed of the fan increased stepwise as the pressure drop across the system increased.

The combustion air was supplied with an external centrifugal fan that was considerably oversized in capacity, but was necessary to supply the required pressure. [This arrangement would not be practical in a production furnace; however, Bratko stated that a small fan with the necessary pressure capability has been developed (ref. 6).] A regulator drops the natural gas supply pressure to 3450 pascals gage (0.5 psig), then the gas is piped through solenoid valves to both a pilot burner and to the main furnace. The pilot burner premixes the gas with part of the combustion air and the mixture is ignited with a spark. A flame rod is used to prove the pilot flame prior to the burner gas solenoid valve opening. The burner gas supply is premixed with combustion air with a mixing device (in the prototype furnace the amounts of both air and fuel could be controlled independently, although in practice, relatively fixed flow rates would be expected). The premixed gas and air is fed to a plenum inside the surface combustor at a pressure of about 895 pascals gage (0.13 psig) and is forced through the refractory pad to burn on the surface. The refractory is selected to be sufficiently insulating that the plenum temperature remains essentially at ambient, thereby eliminating preignition due to heat feedback.

Analytical Instrumentation

The gas sample for analysis was withdrawn from the flue after the gas had been cooled to 422-475 K in the convective pass of the heat exchanger. The samples are conditioned and analyzed with a similar system to that described earlier (ref. 7). To summarize, the analytical instruments are: 1) oxygen by paramagnetic resonance; 2) CO and CO_2 by non-dispersive infrared (NDIR); 3) hydrocarbon by flame ionization detector; 4) NO by a long path NDIR; and 5) NO and NO_x by chemiluminescence analyzer. The temperature of the flue gas was measured with a dial thermometer and cross checked with a thermocouple.

Range of Variables

The tests were planned to screen the furnace combustion and emission performance over the permissible range of operation. The two variables were fuel flow and excess air level. Since there was some interaction between fuel and air flow in the mixer it was not possible to attain completely comparable input levels. Therefore, three nominal values were used: 16,000, 19,000 and 22,000 watts (55,000, 65,000, and 75,000 Btu/hr, respectively). The excess air range for the first two fuel flows was from 45% down to the point where excessive CO (i.e., > 200 ppm) was formed. For the highest rate the maximum excess air was 25%.

In addition a limited number of tests were run with propane to establish the multi-fuel capability of the unit.

EXPERIMENTAL RESULTS

This section presents a discussion of two specific aspects of the results: 1) emissions; and 2) efficiency.

Emissions Measurements

The primary evaluation of the furnace performance was based on measurements of pollutant species in the flue gases as a function of operating condition. To fully characterize the operating range the excess air level was varied from a high value (i.e., > 25%) down to the point that excessive CO (i.e., > 200 ppm) was being emitted. No hydrocarbons or smoke were observed during the test. The effects of excess air and fuel input are discussed below.

Excess Air. The effect of excess air level on emissions is shown in Figure 2 for a thermal input of 16,000 watts (55,000 Btu/hr). The data shown here were obtained during five different experimental periods covering 4 months and the small scatter in the points shows that the performance was quite repeatable. At 40% excess air, the CO emissions are quite low (i.e., 20-30 ppm) and remain low as the excess air is reduced to 10%. When the excess air is reduced below 10% the CO begins to rise sharply and at 5% excess air is greater than 1500 ppm. The results for oxides of nitrogen are shown as measured for both NO and NO_x and corrected to zero % excess air for both NO and NO_x. The NO_x concentration to zero % excess air gives a direct indication of the trend of mass emissions as a function of excess air and will be used as the primary basis of discussion. The NO_x is low (i.e., 7.5 ppm) at 40% excess air and rises slowly to 10 ppm as excess air is decreased to about 15%. Then as excess air is reduced further, the NO_x rises sharply to about 19 ppm at 7.5% excess air. Comparison of the as measured values of NO and NO_x (where the difference is interpreted as being NO_2) shows that the amount of NO_2 increases as the excess air is decreased; however, the ratio of NO_2 to NO is approximately constant. This holds true even when high CO levels are observed.

Fuel Input. The effect of fuel input on emission performance was examined. The furnace design condition was taken as a nominal 16,000 watts (55,000 Btu/hr) and two higher levels were evaluated: 19,000 and 22,000 watts (65,000 and 75,000 Btu/hr, respectively). The data for these higher levels are shown in Figures 3 and 4. The emission trends are essentially the same as the baseline case with only small changes. The point at which CO emissions increase sharply is moved down to 5% excess air for both higher heat inputs. The NO_x emissions are increased slightly as heat input increases for excess air levels of 10 to 30%; however, the ends of the range do show minor differences. Finally, the ratio of NO_2 to NO decreases as the heat input increases.

Fuel Type. A limited series of runs were performed using propane as the fuel. In general, the effect of excess air on emissions was similar to that for natural gas, except that the onset of excessive CO occurred at somewhat higher excess air (i.e., 10-15%). A run with propane at a nominal 26,000 watts (90,000 Btu/hr) heat input gave a different trend as shown in Figure 5. The onset of CO formation occurs at a higher excess air and, of more interest, the ratio of NO_2 to NO increases significantly as the CO begins to increase.

Thermal Efficiency

The data gathered for evaluation of the furnace emission performance can also be used to gain some insight into the thermal efficiency of the furnace. In addition, several measurements of furnace warm air output were made. These two indications of the furnace thermal performance are discussed.

Stack Heat Loss. The main energy loss from a furnace is in the sensible and latent heat associated with the flue gas components, principally N_2, CO_2, O_2 and H_2O. The latent heat loss is determined by the carbon to hydrogen ratio of the fuel and is irretrievable unless a condensing heat exchanger is used. It should be noted that condensing heat exchangers for this application are not currently available. For natural gas the latent heat is equivalent to about 10% of the gross heating value. The sensible heat losses can be minimized by low excess air operation and the lowest stack temperature consistent with avoiding condensation (i.e., about 180 K net). A generalized plot of efficiency versus excess air with stack temperature as a parameter is shown in Figure 6 for natural gas.

The flue gas temperature taken during the experimental runs were relatively independent of excess air for a given firing rate; however, the temperatures increased with increased firing rate. The average flue gas temperatures were 447, 475 and 498 K, at 16,000, 19,000 and 22,000 watts, respectively. An operating excess air of 15% is selected based on the emission curves, giving steady state furnace efficiencies for the three firing rates of 83.4, 82, and 81%, respectively. When the casing losses are taken into consideration, the actual heat loss would be about 2% greater. At the low firing rate, the stack temperature was below the value required to prevent condensation and a production furnace would require less convective heat transfer surface. For the high firing rate, the stack temperature potentially could be reduced by about 22 K. If heat exchanger design was changed to achieve a 475 K stack temperature for each firing rate, the theoretical efficiencies would be the same as that for the 19,000-watt heat input. However, a given furnace is normally designed to be capable of a range of firing rates, and the existing design represents a reasonable compromise for input over 19,000 watts.

Some measurements of output air velocity and temperature rise were made at the output of the plenum on top of the furnace. As an extended duct run was not used to smooth the flow, the stratification of flow due to the heat exchanger was significant. Measured exit velocities were 1.25 to 11.5 m per sec (250 to 2300 ft/min) across the exit face of the plenum, and low temperature rises were normally associated with low velocity areas. These stratifications also strongly influence the accuracy of the measurements; however, they can be taken as semi-quantitative. The warm air flow was about 0.45 m^3/sec for two firing rates, with average temperature rises of 24 and 31 K for heat inputs of 19,000 and 24,000 watts, respectively.

Discussion of Results

Examination of the experimental results raises several points that merit further discussion. It is obvious that some additional measurements within the combustion chamber would greatly assist in explanation of the phenomena involved; however, the fact that the furnace was a prototype inhibited making the modifications required for sampling.

Operating Principle. The inventor of the furnace stated (ref. 6) that the furnace was designed to operate with a hot refractory surface as a means of increasing the radiative heat transfer to the heat exchanger. The use of radiative heat transfer for combustion zone heat removal is a common feature of large conventional boilers with diffusion flame burners (especially the water-tube type); however, in general residential systems do not have heat transfer surface in the combustion zone. It appears that the key features of the design are: 1) the insulating properties of the refractory used to form the surface combustor; and 2) the use of radiative heat transfer to reduce the refractory surface temperature to a level where degradation does not occur. The refractory material was selected to have a low thermal conductivity and, therefore, a very slow soakback of heat from the reacting surface to the plenum containing the premixed fuel and air. It appears that this has a two-fold benefit: 1) the heat release is maintained in a thin zone close to the outside of the refractory surface; and 2) radiative heat transfer reduces the refractory surface temperature to a level where degradation does not occur. The degradation of the refractory with time, and the attendant increase in probability of autoignition, needs to be evaluated.

The use of radiative heat transfer allows a high rate of energy removal and apparently maintains the surface temperature well below the adiabatic temperature for the fuel and air stoichiometry being used. This allows the use of fuel/air ratios near stoichiometric where the adiabatic temperature is about 2200 K (3500°F), and yet the reaction zone temperature is maintained below the level where degradation of the refractory would occur. In addition, the temperature is low enough to reduce thermal NO formation.

The observations of the effect of heat input on combustor performance indicate that some increase in surface temperature may occur with increased fuel input as indicated by the lower excess air capability. This is a relatively small effect that may be associated with either the temperature or the thickness of the heat release zone. The small increase in NO_x level suggests that the change is relatively small. It appears that the increased heat release is balanced by increased radiative transfer and/or an increased convective removal of energy due to the larger volume of combustion gases at a given excess air level. The effects could be explained either on the basis of complete reaction of the fuel within the surface or on the basis of partial reaction in the surface with oxidation being completed by homogeneous reactions in the space between the surface and the firebox wall. To answer these questions fully would require measurement of: 1) surface temperatures for the heat exchanger and the refractory material; 2) gas temperature at the firebox exit; and 3) gas phase species measurements within the firebox.

Based on the foregoing discussion and operating experience with two different combustor and firebox configurations in Bratko prototype furnaces, it appears that proper matching of the combustor and radiative heat transfer surface does significantly influence the performance.

NO_2 Emissions. As noted in the background section, above, instances where the NO_2 is greater than 25% of the NO_x have been observed by several investigators for natural gas combustion under conditions where CO levels are high. This same trend was observed for an earlier version of the Bratko prototype tested for both methane and propane at low excess air (i.e., < 20%). Due to the fuel/air mixer configuration of the earlier furnace, excess air was changed by increasing fuel flow at a relatively constant air flow. With the new furnace, propane at a high fuel rate exhibited a high NO_2 to NO ratio at low excess air. This effect was not noted with the new furnace burning methane even at relatively high firing rates; however, the excess air level at which CO increased was significantly lower (i.e., < 6%).

Although there is some controversy over his interpretation, Merryman (ref. 8) has reported "flame front NO_2" for flat flames. His data show conditions within the reaction zone where NO_2 is a large percentage of the NO_x. This is also the zone in which significant amounts of CO were present. Although a flat flame is difficult to relate directly to a surface combustor, these results give a possible basis for explaining the furnace data. It can be postulated that for a given combustor surface and heat exchanger area, the total oxidation occurs in or very near the surface until some critical fuel flow rate is reached and the final oxidation of fuel fragments (e.g., CO) begins to occur in the gas phase above the surface. At low excess air levels, the combustion may not be completed fast enough by these gas phase reactions, thereby allowing some pockets of gases containing CO and high NO_2 to NO ratios to escape and be quenched before the NO_2 can relax back to NO. If this is the case, the data would tend to indicate that this phenomenon is sensitive to the relationship between the surface combustor and the radiant heat exchanger firebox.

Efficiency. Although the furnace efficiency is good for all the cases tested, the potential exists for optimizing the furnace for each heat input value by fine tuning the convective section of the heat exchanger to get minimum allowable stack temperature. Other features of the furnace may provide an increase of cycle average efficiency, particularly by reducing or eliminating off-cycle losses. One source of such loss is the continued flow of draft air through the firebox during the off-cycle. This not only removes accumulated heat from the furnace components, but may also cause a loss of heated air from the furnace space. The Bratko design provides a positive air shut off, which should reduce off-cycle losses significantly.

CONCLUSIONS

Based on the furnace evaluation the following conclusions can be drawn:

1. The surface combustion concept shows clear potential for NO_x emissions significantly below previously reported values, while also giving low levels of CO and HC.

2. The Bratko furnace represents an application of surface combustion to a practical system once a satisfactory combustion air source is incorporated.

3. The low excess air capability gives the potential for high efficiency. Other furnace features which limit off-cycle losses also have the potential for increasing cycle average efficiencies.

4. The concept appears to lend itself to a wide range of firing rates. In fact, performance improved with natural gas at the higher firing rates tested.

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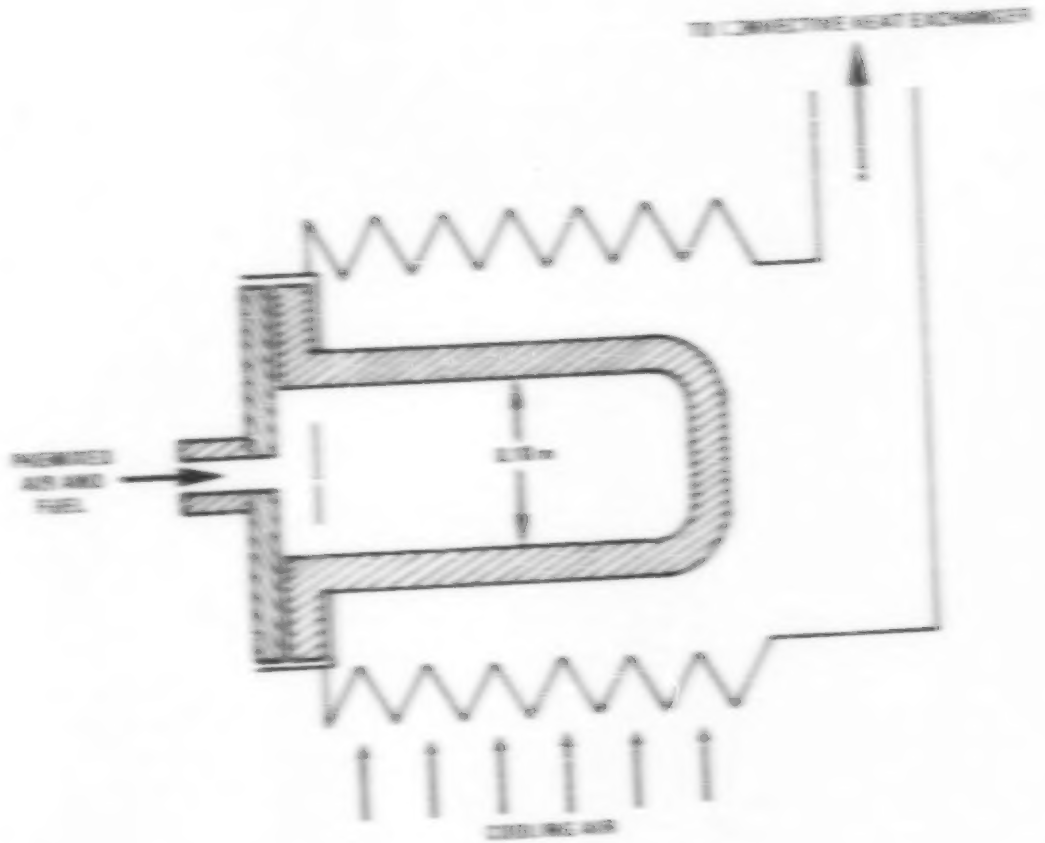

TO CONVECTIVE HEAT EXCHANGER
PREMIXED AIR AND FUEL
0.15 m
COOLING AIR

Figure 1. Sectional view of surface combustor and firebox.

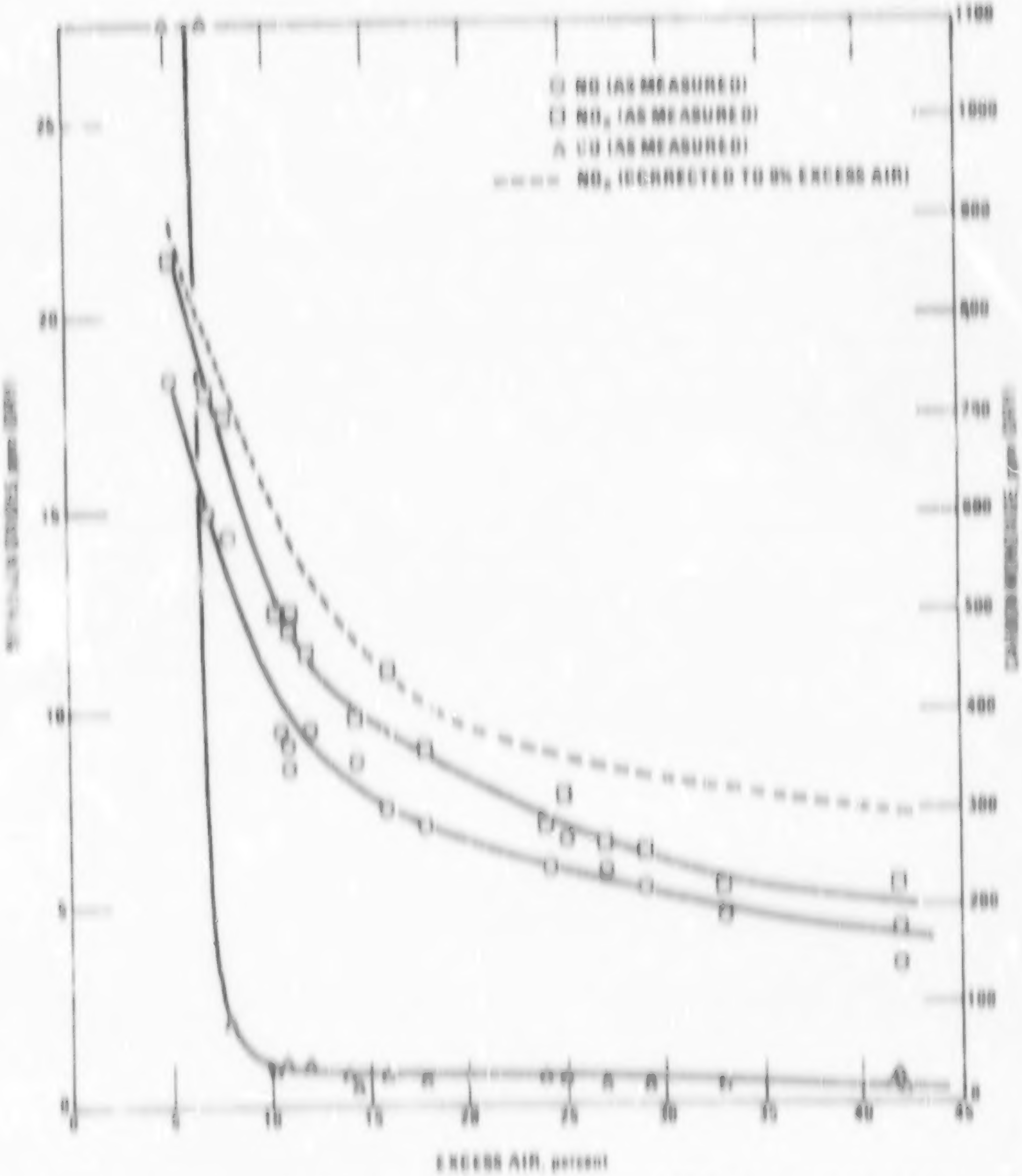

Figure 2. Emissions characteristics at a nominal heat input of 16,000 watts of natural gas

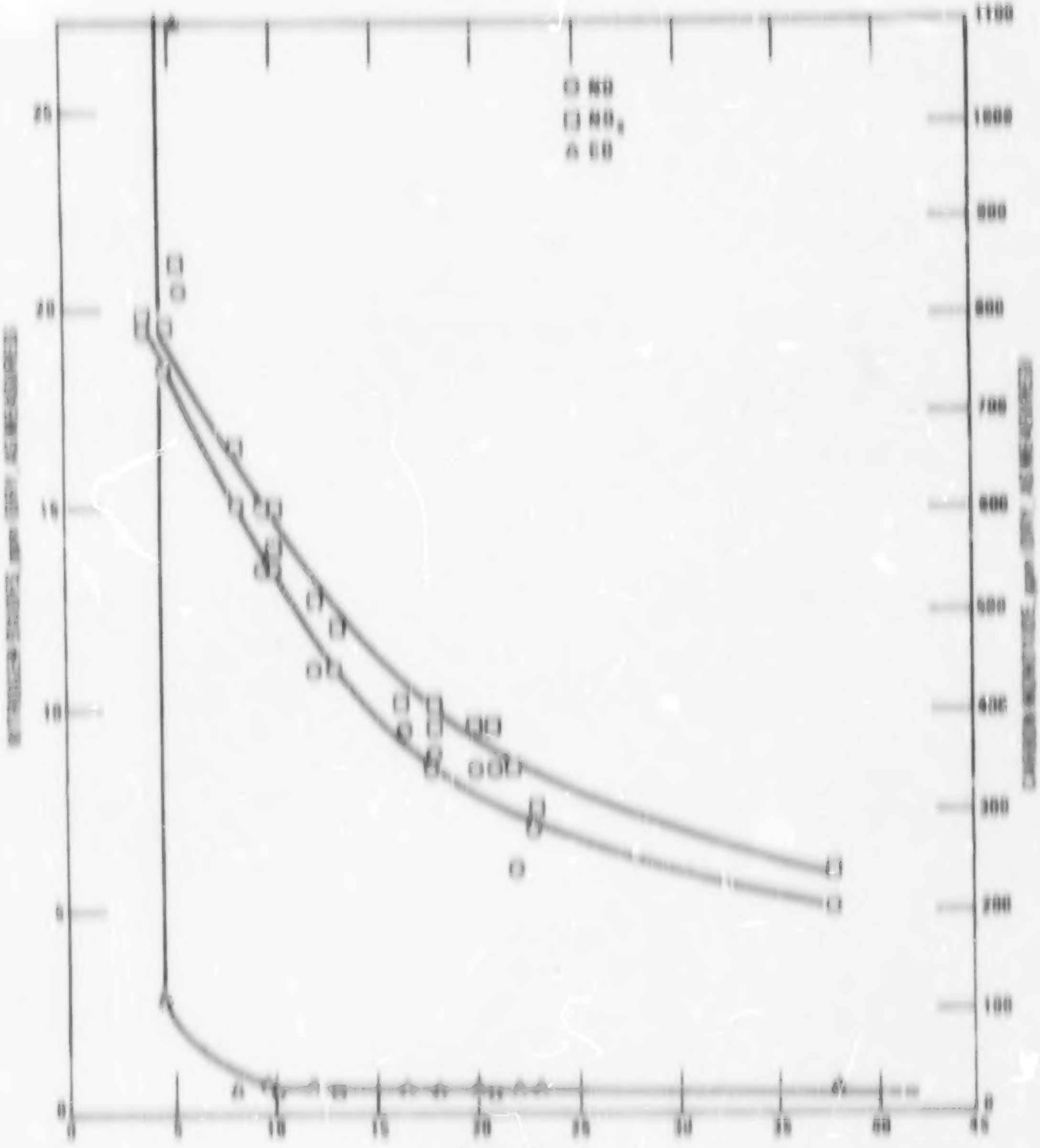

Figure 3. Emission characteristics at a nominal heat input of 19,000 watts of natural gas.

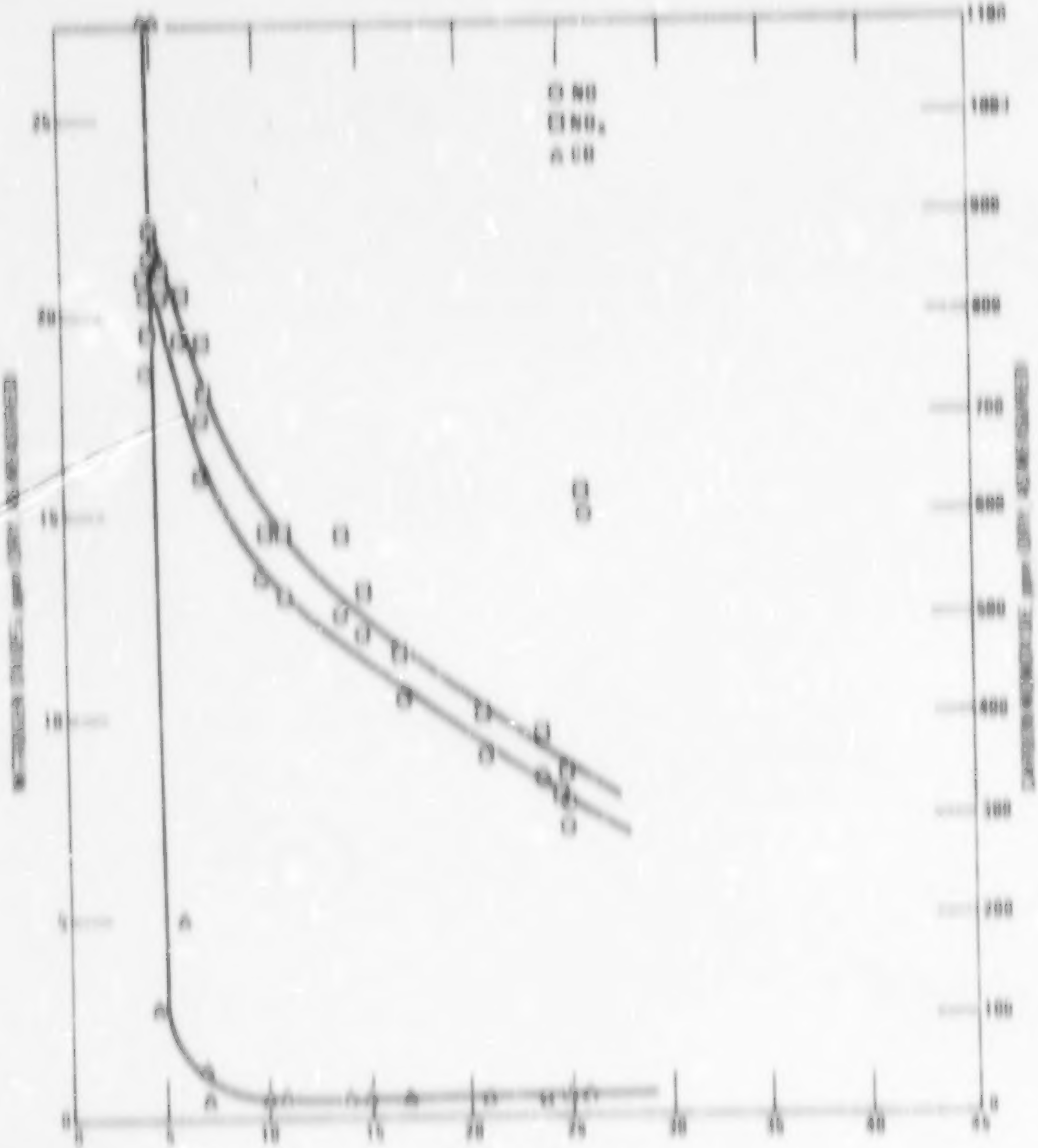

Figure 4. Emission characteristics at a nominal heat input of 22,000 watts of natural gas

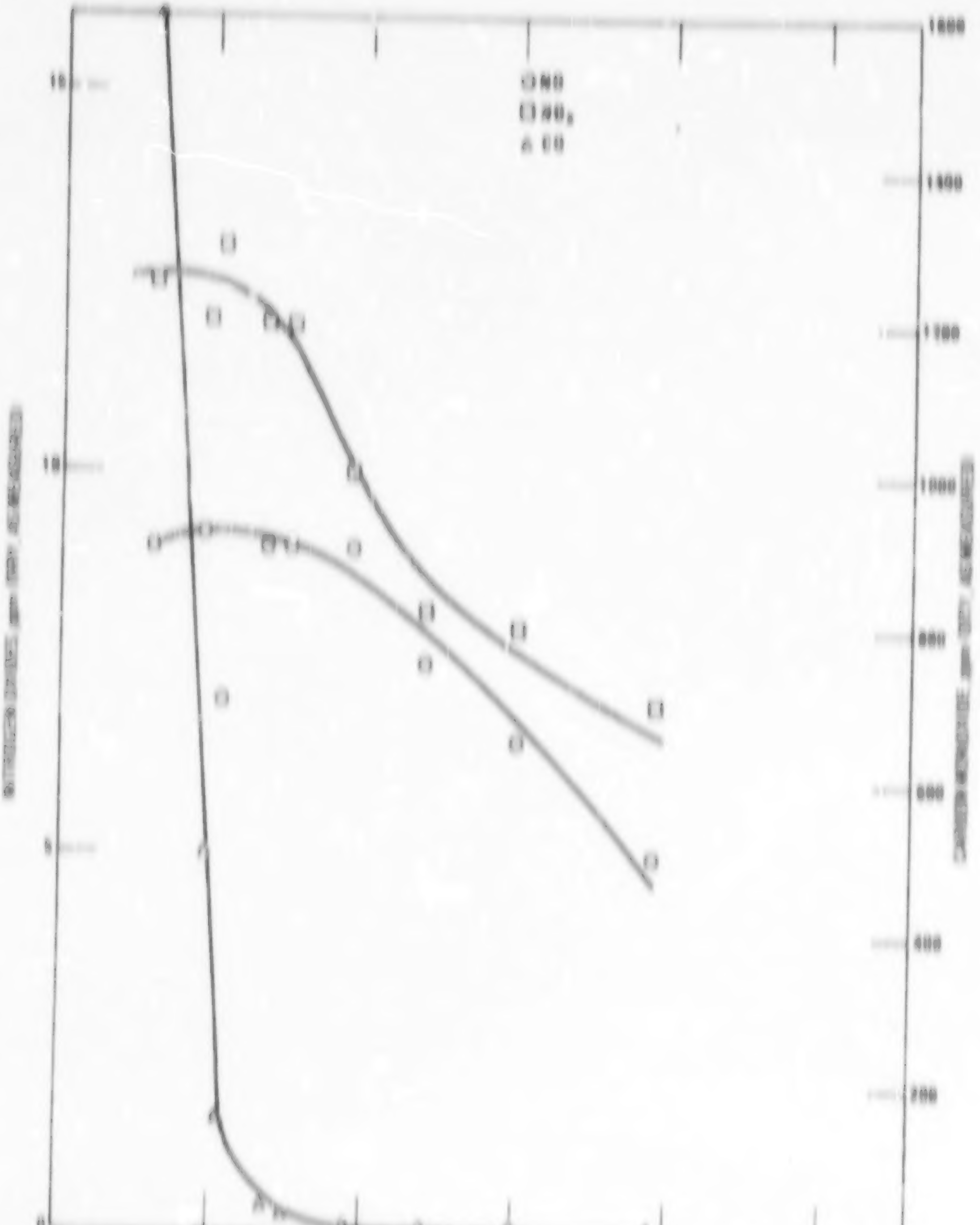

Figure 5. Emission characteristics at a nominal heat input of 26,000 watts of propane.

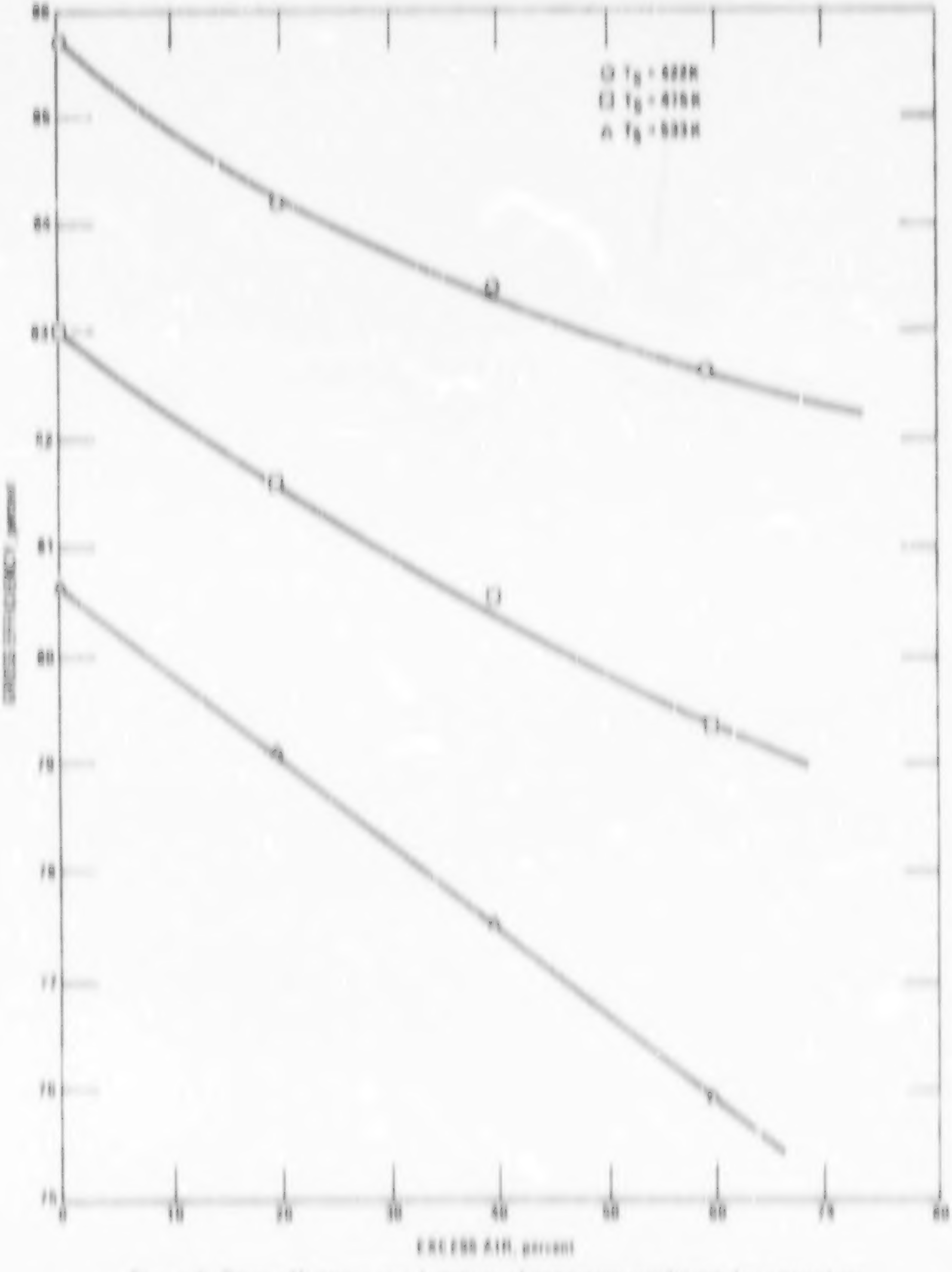

Figure 6. Gross efficiency as a function of operating conditions for natural gas

PANEL: EMERGING COMBUSTION TECHNOLOGIES

1 -- Fluidized Bed Combustion
John M. Connell

2 -- Magnetohydrodynamics
William Jackson

3 -- Coal-Oil Slurries
Casters B. Foster

4 -- Advanced Combined Cycles
Fred Robson

Panel discussion abstracts will be included in Volume V.